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THE MUTUAL AFFINITIES OF THE SPECIES OF THE GENUS CAMBARUS, AND THEIR DISPERSAL OVER THE UNITED STATES.

(PLATE III.)

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In a previous study of the geographical distribution of the crayfishes of the United States (see *Proc. Amer. Phil. Soc.*, xli, 1902, pp. 277–385), the present writer took it for granted that the division of the genus *Cambarus*, into five groups, as introduced by Faxon (*Mem. Mus. Harvard*, 10, 1885), and the arrangement of the species within each group adopted by him, would correspond, as far as one might expect, to the natural affinities.

This, however, is true only to a certain degree. There is no doubt that Faxon correctly recognized the chief systematic groups within the genus, and that he also had, in most cases, appropriate views as to the relationship of smaller groups of species. But accepting his system as a whole, and trying to correlate it with the peculiarities shown by the geographical distribution, a number of cases are revealed, where such a correlation is not very apparent, and attempts to give a reasonable theoretical explanation prove to be more or less unsatisfactory. I shall mention here a few instances.

1. The fifth group of the genus follows, in Faxon's system, after

the fourth, and he apparently believes, that it is connected genetically with the latter. The geographical distribution, however, is opposed to this assumption, and a closer study has led me to think that there is no such affinity between these two groups, and that the fifth is more closely allied to the first and second. (Compare Ortmann, *l. c.*, 1902, p. 283.)

2. Faxon believes (*l. c.*, 1885, p. 19) that the first group contains the most primitive forms. This is not probable when we consider the very highly specialized character of most of the species. Indeed, there are rather primitive forms among them, but they are clearly not as primitive as certain species of the second group (Ortmann, 1903, p. 283), and further, the main range of the first group occupies a territory that is, geologically, comparatively young, namely, the lowlands of the southern states (Mississippi, Alabama, Georgia, Florida), of which we know that they became land by degrees during the Tertiary period, the more southern parts in very recent times. It is not very likely that this recent land is occupied by an ancient group of animals.

3. I strongly object to placing *Cambarus pellucidus*, the blind cave-species of Kentucky and Indiana, with the first group, where it stands entirely isolated, morphologically as well as geographically. If we place this species at the beginning of the fourth group, it comes into an assemblage, from which it is not so strongly different. It will always remain a remarkable, and, as Faxon believes, a primitive type, but it is not *the most primitive* type of the genus in all respects. In the shape of the male organs it certainly points rather to the fourth group than to the first.

4. Faxon places *C. blandingi* at the head of the genus: this is apparently due to the desire to let the type-species of the genus stand first. This, however, may convey the wrong impression, that *C. blandingi* is the lowest (or else the highest) form of the whole genus. But I do not think that it is either, and regard it as a highly specialized (but not *the most highly* specialized) form of a branch of the genus that is rather ancient. The distribution of *C. blandingi* has all the characters of a comparatively modern encroachment upon foreign territory.

5. I believe that the second group of Faxon contains the most primitive types of the genus. But this is to be understood "cum grano salis." There are, in this group also some very highly

specialized types (*C. gracilis* and allies), and even some of the primitive forms (*C. cubensis*) possess some peculiar and apparently advanced characters. I think we can express it this way: among the second group, there are species that approach most closely the original stock of the genus, but they themselves are modified to a degree. If I am to single out a species that possibly is *the* most primitive, I should name *C. digueti* Bouvier (*Bull. Mus. Paris*, 1897, p. 224), which is identical with *C. carinàtus* Faxon (*Pr. U. S. Mus.*, 20, 1898, p. 648). It is remarkable that the most primitive forms are found in Mexico (and Cuba), which agrees well with the theory of the origin of the genus in these parts (see Ortmann, *l. c.*, 1902, p. 283).

CHARACTERS OF THE GENUS CAMBARUS THAT SERVE TO DISTINGUISH GROUPS AND SPECIES.

Sexual Organs. — Already the earlier writers (Girard, Hagen) have pointed out the importance of the anterior pair of abdominal appendages of the male (copulatory organs) for systematic purposes. Faxon made large use of them in defining his five groups, but within the groups he rarely tried to avail himself of these limbs to reveal the mutual affinities of the different species. It is now generally known that these organs furnish not only the best specific characters, but that their similarity in certain assemblages of species clearly indicates genetic relationship. In close connection with the shape of this organ is that of the female "annulus ventralis," as we now know, the receptaculum seminis. There is, however, not so much variety in the shape of the latter organ, it is not so polymorphous, and the main types occur in different groups, which is apparently due to the more simple structure of this organ. Nevertheless, the annulus — in connection with the male organ — is rather important. We may add that in a number of species the annulus is not very well known.

As regards the male organs, their shape is very complex and much varied. Several main types may be distinguished, and these again show much diversity. It is hardly likely that in so complex an organ the identical form has developed several times, that is to say that there are cases of parallelism; where there is identity or similarity of these organs in different species, this is generally and surely a sign of close affinity. Only one or two exceptions in the

first and second group are known to me, where the question is admissible, whether convergency plays a part. There are rarely two species known, where the shape of the male organs is absolutely identical (except in the third group of Faxon, where they are remarkably uniform), and since they have developed from the beginning in three or four different main lines, it is easily understood why they furnish the best specific characters as well as the best criteria for judging the affinities. Thus the danger of being misled by convergency of structure, which is the chief impediment of properly recognizing natural affinities in any group of animals, is here reduced to a minimum. We shall see below that by the actual use of this principle we arrive at conclusions that render the investigation of the development of the genus *Cambarus* a comparatively easy task, furnishing a clue to the explanation of the geographical distribution; further, the study of the male organs gives us a standard by which to judge the other characters that are of systematic value, and as we shall presently see, there is hardly another structure that has the same value for revealing the affinities within the genus, that is to say, the same characters generally develop independently in different groups, being clearly subject to parallelism, presumably under the influence of similar external conditions. In a few cases the latter is very evident.

Copulatory Hooks of the Male.—Faxon lays much stress upon the number of hooks present in the male on the ischiopodite of the second, third, or fourth pereiopods, which are used to take hold of the female in copulation. The third pereiopods always possess these hooks, and in many cases only this pair is present. But sometimes there is an additional pair on the second, or on the fourth pereiopods. The number of pairs of hooks is very constant in the single species (except for occasional abnormities), and it is remarkable that certain types of male sexual organs are generally connected with certain type of hooks; this is chiefly the case in the third, fourth and fifth group of Faxon, while it is not in the first or second, where similar types of sexual organs may be connected with different types of hooks.

If we consider that the presence of two pairs of hooks is certainly a more highly advanced stage than that of only one pair, that is to say, that the difference of the number of hooks is only a difference in the degree of development of one and the same feature, it

is easily conceivable that the increase of the number of hooks may have taken place independently in different groups, and we shall see below that there is at least one case (*C. pellucidus*), where we are to assume an independent origin of an additional pair of hooks on the fourth pereiopods; this is also rendered probable by the variability of this character seen in this species. That Faxon's fifth group has developed an additional pair of hooks independently is clearly shown by the fact that here it is the second pair of pereiopods that carries the additional hooks.

Indications of a more general tendency to increase the number of hooks are found in occasional freaks in other groups (*C. propinquus*, *C. virilis*).

General Shape of Carapace. — The primitive type of the carapace seems to be more or less ovate, generally depressed. It assumes, however, sometimes a more cylindrical form (in some cave-species), and in some cases it is rather compressed. The latter character is most remarkable in all burrowing species, and has developed independently at least in two groups (second and third of Faxon, *gracilis*- and *diogenes*-groups).

The *Areola* seems to be originally rather broad and short. But there is a general tendency of it to become narrower, and at the same time to increase its relative length. This is evidenced in almost all groups, and a narrow, sometimes partly obliterated areola is found in species that have nothing whatever to do with each other. In fact, it is only the fifth group of Faxon where this tendency is not manifested. Generally, the length of the areola is correlated to the width, but there are exceptions.

Rostrum. — The shape of the rostrum is characteristic for most species, but it is available only as a specific character. The original type seems to be a rather long rostrum, with more or less parallel margins, with a marginal spine on each side, and a rather long acumen. The chief tendency in further development is for the marginal spines to disappear, and for the whole rostrum to become shorter. This, however, is found in all five groups of Faxon in species which are not at all allied to one another. Even certain peculiar types of rostrum may reappear in a widely divergent group. Thus the *blandingi*-type is imitated, if the expression is permitted, by *C. immunis*, and the burrowing species possess all a rostrum of similar shape.

[It is very remarkable, that burrowing crayfishes of the southern hemisphere (*Parastacus defossus* Fax. from southern Brazil is at hand) resemble the North American burrowing species in a remarkable degree externally, chiefly so in the shape of carapace, rostrum, chelæ, length of abdomen, etc.]

The *Chelæ* are very variable in shape: they are fully developed only in old males, but generally quite characteristic for the species. One and the same type is often common to large groups of species, and thus they are often a good help in the investigation of the natural affinities. But in other cases a similar form of chelæ is found in different groups which is most striking again in the burrowing species.

Among the more primitive species the shape of the chelæ seems to be more or less subcylindrical, and rather elongated. This shape is found in Faxon's first, second, third, and fifth groups, but only in the first, second and fifth it is frequent. Removing *C. pellucidus* to the fourth group, also in the latter this type of chelæ is represented. In part of the second group, and in the third and fourth, a more or less ovate, broad, and depressed chela becomes common, but there is not much uniformity in detail, each group generally developing its own type.

The above are the more important characters. We see that all of them must be dealt with cautiously, if they are to be used for the investigation of affinities of species. Indeed, in many cases, they support the conclusions arrived at by the examination of the the sexual organs, but very frequently similarities of the above characters are due to convergency. The same is true of all other characters, such as armature of carapace, chelæ, shape of epistoma, antennal scales, of abdomen, telson, etc.

SUBGENERA OF CAMBARUS, ACCORDING TO THE CHIEF TYPES OF THE SEXUAL ORGANS OF MALE.

There are three chief types of the male sexual organs (first pair of abdominal appendages), the last of which is easily divided into two subtypes. According to these, I should like to distinguish four subgenera, as follows:

1. Subgenus: CAMBARUS (sens. strict.).

Sexual organs of male *stout*, more or less straight, and comparatively short, *truncated or blunt at the tip, the outer part ending in 1–3*

horny teeth, which are sometimes recurved, or compressed, or plate-like, and are *always sharply distinguishable from the blunt end.* Inner part terminated by a shorter or longer, acute spine, which is sometimes distinct from the tip of this part, so that it appears two-pointed. In the male the third or the third and fourth pereiopods have hooks.

2. Subgenus: CAMBARELLUS nov. subgen.

Sexual organs of male *stout*, straight, or slightly curved at the tips. *Outer part ending in two horny teeth*, which are rather long, taper rapidly, and are *not sharply distinguishable from the end, which is not truncated.* Inner part terminated by a rather long, acute spine. In the male, the second and third pereiopods have hooks.

[The two following subgenera represent the third type of male sexual organs, in which both parts, outer and inner, each terminate in *only one* tooth, which is rather slender, and *not sharply distinguishable* from the end, which is never truncated.]

3. Subgenus: FAXONIUS nov. subgen.

Sexual organs of male shorter or longer, *not very stout, generally slender*, or with slightly curved tips. *Tips never truncated, ending always in two more or less elongated spines*, the one formed by the outer part, and horny, the other formed by the inner part and softer. There is *never more than one tip to the outer part*, and there is no terminal tooth distinguishable, but the tip tapers gradually, or the whole outer part is setiform. In the male generally the third pereiopods only have hooks, very rarely (in *C. pellucidus*) hooks are found on third and fourth pereipods.

4. Subgenus: BARTONIUS nov. subgen.

Sexual organs of male very uniform throughout the subgenus. They are *short and thick*, inner and outer part each terminating in *only one short and thick spine*, tapering to a point. Both terminal spines are *strongly recurved*, forming with the basal part about a right angle. In the male, only the third pereiopods possess hooks.

Subgenus: CAMBARUS. (Type: *C. blandingi.*)

This subgenus comprises Faxon's first and second group, excluding the species *C. pellucidus*. Both groups are rather heterogeneous, and so is this subgenus, and there are considerable variations in the male sexual organs. The chief feature of the latter is their blunt

ending, a character that possibly points to the condition seen in the genus *Potamobius;* for the rest, the terminal teeth are quite variable, but always very characteristic for the species.

It is advisable to distinguish groups within this subgenus, not only with reference to the sexual organs, but also with reference to the hooks of the male, for the presence of one or two pairs of hooks seems to constitute, as already Faxon recognized, important differences, the presence of two pairs, on third and fourth pereiopods, being evidently a more advanced stage. Using in addition some other differences of the areola and the chelæ, we obtain the following three sections.

1. Section: C. digueti.

Sexual organs of male with one to two teeth at the tip of the outer part. Male with hooks on third pereiopods. Areola wide or narrow, but never obliterated, about half as long as the anterior section of the carapace (incl. rostrum), or shorter. Chelæ elongated and subcylindrical.

2. Section: C. gracilis.

Sexual organs of male with one to two teeth at the tip of the outer part. Male with hooks on third pereiopods. Areola obliterated in the middle, considerably longer than half of the anterior section of the carapace. Chelæ short, broad, ovate.

3. Section: C. blandingi.

Sexual organs of male with one to three teeth at the tip of the outer part. Male with hooks on third and fourth pereiopods. Areola wide or narrow, rarely obliterated in the middle, shorter or longer. Chelæ generally elongated, narrow, and subcylindrical.

The most primitive sexual organs are found in species of the first section, where there is only one tooth at the end of the outer part. Similar sexual organs are found in the second (*C. advena*) and in the third section (*C. evermanni*): in the latter cases, however, I think we have to deal with parallelism, the single tooth in both cases being due possibly to reduction. Since these two species are very rare and poorly known, and since *C. evermanni* belongs to a group that offers other difficulties, further investigations are needed.

A closer examination may reveal the fact, that the sexual organs of the *digueti-group* are more sharply distinguished from those of *C. advena* and *evermanni*. Through the courtesy of Professor E. Bouvier of Paris, I have received two cotypes (male and female)

of his *C. digueti*, which show, on the one hand, that *C. carinatus* Fax. is a synonym of this species, and on the other hand, that the sexual organs have a rather peculiar shape. The figures of these organs, given by Faxon (*Pr. U. S. Mus.*, 20, 1898, pl. 63, f. 2 and 3) are absolutely correct, but the description (p. 648) is rather short and unsatisfactory. Faxon says: "Inner and outer parts ending in a small horny tooth, anterior margin furnished with a small tooth near the tip." Fig. 2 represents this organ of the right side, seen from the outside: the outer part ends bluntly, without a distinct tooth, while the inner part ends in a rather pointed tooth, outside of which is a sharp spine that is longer than the outer part. Faxon's Fig. 3 represents the identical part seen from the inside: only the two tips of the inner part are seen here, and the tip of the outer part is hidden behind the end of the inner; the inner part is flattened and hairy on the inside, and the "shoulder" ("small tooth near tip") is distinctly developed. My male specimen of *C. digueti* agrees in every detail with the figures of Faxon.

A very similar structure is seen in *C. cubensis* (Faxon, 1885, pl. 7, f. 5), only here the flattened face of the inside is dilated, and the shoulder is more prominent. In both cases, there are practically three tips to this appendage, *two* of which belong to the *inner* part.

The description of this organ in *C. mexicanus* (Faxon, *l. c.*, p. 50) agrees closely, but possibly the "small, procurved spine" attributed to the external part belongs to the internal, and then there would be complete agreement.

The double tip to the inner part, and the shoulder, which has a very peculiar position, possibly give to these three species a more isolated position within this subgenus, and might possibly justify the creation of a separate subgenus, which then should stand at the head of the genus. This would also agree well with the geographical distribution.

Aside from these more primitive species (*C. digueti*, *cubensis*, *mexicanus*), the first section contains two others (*C. simulans* and *gallinas*), which mark the transition to the third section, from which they differ only by the number of hooks of the male; the third section contains more advanced forms of the *simulans*-type. The second section is a peculiar side branch going off from the first section, which has acquired burrowing habits; this is known posi-

tively of *C. gracilis* and of *C. advena* (Hyeme vitam degit subterraneam. Aestate in fossis invenitur. Leconte).

The large number of species known in the third section makes a further division desirable, which is easily made according to the following characters:

1. *Group:* (*spiculifer*).

Outer part of sexual organs with two or three recurved teeth, without prominent angle (*shoulder*) *on anterior margin. Rostrum with marginal teeth, acumen rather long. Areola wide, rarely narrow, distinctly shorter than half of the anterior section of the carapace.*

2. *Group:* (*blandingi*).

Outer part of sexual organs with three (*rarely two*) *recurved teeth, inner part with terminal spine directed obliquely outward. No shoulder on anterior margin. Rostrum with marginal teeth, acumem rather short. Areola narrow, generally distinctly longer than half of the anterior section of the carapace.*

3. *Group:* (*clarki*).

Outer part of sexual organs with two compressed tubercles, inner part straight, directed forwards. Anterior margin with a distinct shoulder. Rostrum with marginal teeth, acumen rather short. Areola very narrow, often obliterated in the middle, about half as long as anterior section of carapace.

4. *Group:* (*alleni*).

Outer part of sexual organs with one or two teeth, often peculiarly formed (*compressed and plate-like*), *inner part straight or oblique. No shoulder on anterior margin. Rostrum without marginal teeth* (*at least in the adult stage*). *Areola moderately wide, about half as long as anterior section of carapace.*

There is no doubt, that the *spiculifer-group* is the most primitive of these, and that the others represent special modifications, each developed in a different direction.

The following key for the identification of the species of the subgenus *Cambarus* is submitted; it is claimed that this key represents — as far as is possible in a "key" — the natural affinities. If adult males of the first form are at hand, it should be possible, in every case, to correctly identify the species.

1. *Section of C. digueti* (see p. 98).

a_1 Sexual organs of male with only one terminal tooth on outer part, inner part with two tips; anterior margin with an angular projection (shoulder) near the tip (*digueti-group*).

b_1 Rostrum with marginal teeth.

c_1 Sexual organs of male with inner part not broadly dilated on inner side, curved forward at apex ; shoulder small. Rostrum carinated above. Carapace with lateral spines.

C. (*Cambarus*) *digueti* Bouv.

c_2 Sexual organs of male with inner part greatly dilated, forming a broad, flat, setose plate on inner side ; shoulder strongly developed. Rostrum not carinated. Carapace without lateral spines.

C. (*Cambarus*) *cubensis* Er.

b_2 Rostrum without marginal teeth, subplane above. Carapace without lateral teeth. Inner part of sexual organs flattened within, but not greatly dilated. *C.* (*Cambarus*) *mexicanus* Er.

a_2 Sexual organs of male with two terminal teeth on outer part, one of which is flat and disk-shaped, inner part with one terminal spine ; without shoulder on anterior margin. Rostrum without marginal teeth (*simulans-group*).

b_1 Terminal teeth of sexual organs oblique, both of about the same length Acumen of rostrum longer. *C.* (*Cambarus*) *simulans* Fax.

b_2 Terminal teeth of sexual organs straight, one much longer than the other. Acumen of rostrum shorter. *C.* (*Cambarus*) *gallinas* Cock. and Port.

2. *Section of C. gracilis* (see p. 98).

a_1 Rostrum suddenly contracted into a short acumen. Sexual organs with two teeth at end of outer part. Terminal spine of inner part straight, longer than outer part.

b_1 Anterior margin of carapace forming a blunt suborbital angle.

C. (*Cambarus*) *gracilis* Bund.

b_2 Anterior margin of carapace not forming a suborbital angle.

C. (*Cambarus*) *hagenianus* Fax.

a_2 Rostrum triangular, margins not suddenly contracted to form an acumen. Sexual organs with only one compressed, triangular tooth at the end of outer part. Inner part straight, not longer than outer.

C. (*Cambarus*) *advena* (Lec.).

3. *Section of C. blandingi* (see p. 98).

1. *Group of C. spiculifer* (see p. 100).

a_1 Areola wide. Chelæ rather broad. Two lateral spines on each side of the carapace.

b_1 Chelæ with large, remote tubercles. Margin of rostrum converging. Outer part of sexual organs with two terminal teeth.

C. (*Cambarus*) *spiculifer* (Lec.).

b_2 Chelæ with small, crowded tubercles. Margins of rostrum subparallel. Outer part of sexual organs with three terminal teeth.

C. (*Cambarus*) *versutus* Hag.

a_2 Areola wide or narrow. Chelæ generally narrower. One lateral spine on each side of the carapace.

b_1 Rostrum subplane above, ciliated. Areola wide. Outer part of sexual organs with two terminal teeth, the inner part with terminal spine directed outward. *C.* (*Cambarus*) *pubescens* Fax.

b_2 Rostrum concave above, smooth. Areola narrower.

c_1 Margins of rostrum subparallel. Outer part of sexual organs with two terminal teeth, the inner part straight.

C. (*Cambarus*) *angustatus* (Lec.).

c_2 Margins of rostrum convergent. Outer part of sexual organs with three terminal teeth, the inner part directed outward.

C. (*Cambarus*) *lecontei* Hag.

2. *Group of C. blandingi* (see p. 100).

a_1 Eyes rudimentary. Outer part of sexual organs with two terminal teeth.

C. (*Cambarus*) *acherontis* Loennb.

a_2 Eyes well developed. Outer part of sexual organs with three terminal teeth.

b_1 Sexual organs straight, terminal teeth well developed.

c_1 Sexual organs not excavated on outer side near distal end.

C. (*Cambarus*) *blandingi* (Harl.)

c_2 Sexual organs excavated on outer side near distal end.

C. (*Cambarus*) *hayi* Fax.

b_2 Sexual organs curved back distally, terminal teeth minute.

C. (*Cambarus*) *fallax* Hag.

3. *Group of C. clarki* (see p. 100).

a_1 Rostrum concave above, acumen slightly longer. Shoulder of sexual organs slightly developed. *C.* (*Cambarus*) *clarki* Gir.

a_2 Rostrum plane above, acumen shorter. Shoulder of sexual organs very prominent. *C.* (*Cambarus*) *troglodytes* (Lec.).

4. *Group of C. alleni* (see p. 100).

a_1 Outer part of sexual organs with one or two terminal teeth; inner part not longer than the outer. Hooks of fourth pereiopods of male not bituberculate.

b_1 Rostrum concave above. Outer part of sexual organs with one recurved terminal tooth; inner part with the terminal spine placed obliquely.

C. (*Cambarus*) *evermanni* Fax.

b_2 Rostrum plane above. Outer part of sexual organs with terminal part plate-like, covering the inner part, and with two very small teeth.

c_1 Chelæ bearded on inner margin. *C.* (*Cambarus*) *barbatus* Fax.

c_2 Chelæ not bearded on inner margin.

C. (*Cambarus*) *wiegmanni* Er. (?).

a_2 Outer part of sexual organs forming at apex a broad, flattened plate, whose anterior margin is furnished with hairs and one strong seta, the posterior margin of the plate produced anteriorly into a blunt process. Inner part produced into an erect spine, which is much longer than the outer part. Hooks of fourth pereiopods of male bituberculate.

C. (*Cambarus*) *alleni* Fax.

Note: The position of *C. wiegmanni* is very doubtful, since the male sexual organs are unknown. It has been placed with *C. barbatus* by Hagen and Faxon, but only the external resemblance to

this species speaks for its position here. The geographical distribution, however, is entirely opposed to it, and I very strongly suspect that it belongs somewhere else.

GEOGRAPHICAL DISTRIBUTION OF THE SUBGENUS CAMBARUS.

Taken as a whole, the subgenus *Cambarus* occupies a rather continuous area, with a possible interruption in northern Mexico: this gap, however, may be due only to the incompleteness of our knowledge. It covers Mexico, and a large part of the southern, central and eastern United States, but leaves unoccupied the mountainous region of the East; it is lacking in the larger part of Tennessee, in Kentucky, West Virginia, Pennsylvania, and northward. The largest number of species is found in the southeastern states: Mississippi, Alabama, Georgia, and this region represents at present the center of frequency of the subgenus. From here it extends, gradually declining, westward into Texas, northward up the Mississippi valley, becoming quite scarce north of the State of Missouri (only two species), and further it has populated the Atlantic coast plain as far north as New Jersey (only one species north of South Carolina).

Regarding the single sections, the distribution shows rather peculiar features. The *digueti-section* is characterized by a marked discontinuity: two species are found in Mexico, one in Cuba, and two in New Mexico, Texas and Kansas. Since I consider this section the most primitive of the genus, this discontinuity is highly interesting, and tends to confirm this view. And further, this peculiar distribution probably indicates the direction of the immigration into the United States. The most primitive forms (*C. digueti* and *mexicanus*) are still preserved in the original home of the genus, in Mexico, while two other, somewhat more advanced species (*C. simulans* and *gallinas*) occupy the higher plains lying to the east of the Rocky Mountains in the southwestern United States. These parts are largely formed by Cretaceous deposits, and represent the first land-connection between western and eastern North America after the Upper-Cretaceous separation. It is very significant, that just these parts contain the most primitive forms of the United States, and thus the distribution of the *digueti-section* clearly indicates this old condition prevailing at the end of the

Cretaceous and the beginning of the Tertiary time, and also gives a clue as to the direction of the migration: it did not go over the lowlands of Texas, which are geologically younger, but over the higher plains of the interior. (See Ortmann, 1902, pp. 282–285, p. 388.)

The *gracilis-section*, which is a specialized type, arising from the more primitive forms of the subgenus, forms in the distribution of the species *C. gracilis* a direct continuation of this southwestern range of the *digueti-section*: *C. gracilis* is found from eastern Kansas through Missouri, to Illinois, Iowa, and southern Wisconsin. This is in the same line of the migration marked by the distribution of the species of the *digueti-section*, and plainly its continuation in a northeastern direction. However, the two other species of the *gracilis-section*, *C. hagenianus* and *advena*, are entirely isolated, being found only far in the east, in the lowlands of Georgia and South Carolina. Here again we have discontinuity, indicating old age. I have no doubt, that these separated localities once were connected, namely from Kansas and northern Texas over Arkansas and across the Mississippi valley into Mississippi, and the northern, higher parts of Alabama and Georgia, including probably Tennessee.

Thus I think that the most primitive forms of *Cambarus* occupied, in the United States, first the Cretaceous plains of the southwest, necessarily reaching in very early times the Ozark Mountains, following the Ozark uplift into Illinois and beyond, and, on the other hand, crossing the present Mississippi valley, and reaching the southern end of the Appalachian system, and finally the sea coast in Georgia and South Carolina. Representatives of the primitive sections of the subgenus have now disappeared in the Appalachian region, and this is very likely due to the fact, that, as we shall see below, just in this region some other very vigorous groups developed, which apparently suppressed those earlier forms. In the southwestern extremity, where these new groups are rather scarce or entirely lacking, there was a chance for the old types to survive, and this may account for the presence of *C. simulans* and *gallinas* in this region, while *C. gracilis*, which is found right in the chief domain of the subgenus *Faxonius*, survived possibly on account of its different habits. For similar reasons *C. hagenianus* and *advena* may have survived at the extreme eastern seashore.

The *third* section of the subgenus *Cambarus* represents typically

the distribution of the whole subgenus, with the exception that it is not found in the extreme west and in Mexico. (I disregard *C. wiegmani*, since I do not believe that its position with this section is correct.)

Here again we have peculiar facts of distribution. The more primitive forms (*spiculifer-group*) are restricted to the states Georgia, Alabama, and northwestern Florida. Thus they come into close contact with the hypothetical old range of the more ancient types of the subgenus in the southern Appalachians, and I believe that they originated from an original stock of the *digueti-section*, that immigrated into the lowlands south of the mountains, which became dry land by degrees during Tertiary times. Here in these lowlands, chiefly in Alabama and Georgia, is the center of origin of the *blandingi-section*, which represents a secondary center for the subgenus. The more primitive forms (*spiculifer-group*) still stick to this center, while the more advanced forms have spread out from here as follows.

The *blandingi-group* invaded (*C. fallax*) northern Florida, and spread out northeastwardly along the Atlantic coast plain (*C. blandingi-typicus*), and also it migrated westward aud northward, up the Mississippi valley (*C. hayi* and *blandingi acutus*). The *clarki-group* extended chiefly westward from northern Florida far into Texas (*C. clarki*), and slightly eastward into South Carolina (*C. troglodytes*, in South Carolina and Georgia). Finally, the *alleni-group* occupied Florida: *C. alleni*, the most aberrant form, goes farthest south here (Caloosahatchee River, Lee Co.). (The other species, *C. evermanni* and *barbatus*, are known from scattered localities in Georgia, western Florida, and Mississippi, and their distribution needs further investigation; *C. wiegmanni* from Mexico possibly does not belong here.)

Thus the distribution of the subgenus *Cambarus* illustrates the early history of the immigration of the genus into the United States, and it also illustrates the later population of the southern parts of the United States during Tertiary times by forms of the *blandingi-section*. The latter prevail here, and hardly ever had any competitors, and thus the southern states are at the present time the center of the frequency of the whole subgenus. They are, however, the center of origin only for the *blandingi-section*, while the center of origin of the subgenus is to be sought in Mexico.

The more advanced forms of the subgenus *Cambarus* generally seem to prefer the ponds, lakes, and sluggish streams of the lowlands.

Subgenus: CAMBARELLUS (Type: *C. montezumæ*).

This subgenus corresponds to the fifth group of Faxon.

Faxon compares the male sexual organs with those of his fourth group (= *Faxonius*), but I rather think that they are more closely allied to those of his first and second group (= subgenus *Cambarus*). This latter relation, with the more primitive forms of the subgenus *Cambarus*, is confirmed by other characters: carapace and areola which are rather primitive, at least not very highly advanced; the rostrum has lateral teeth, which show a tendency to disappear; the chelæ are very simple, more or less elongated and subcylindrical, which is distinctly a primitive feature. The annulus ventralis of the female seems to be very remarkable in *C. montezumæ* (movable, fixed only at the posterior end), and also in *C. shufeldti* (a transverse curved ridge, the hind side of the ridge concave).

The three species of the subgenus may be distinguished as follows:

a_1 Sexual organs of male with straight terminal teeth. Carapace with lateral spines. Rostrum with distinct marginal spines.

C. (*Cambarellus*) *shufeldti* Fax.

a_2 Sexual organs of male with curved terminal teeth. Carapace without lateral spines. Rostrum with or without marginal spines.

b_1 Carapace slender and subcylindrical. Rostrum longer and narrower, with sharp marginal spines, and long, spiniform acumen.

C. (*Cambarellus*) *chapalanus* Fax.

b_2 Carapace ovate. Rostrum shorter and wider, with or without marginal spines, in the first case, the acumen is much shorter.

C. (*Cambarellus*) *montezumæ* Sauss.

C. shufeldti is apparently more primitive than the other two species. I have no doubt that *Cambarellus* took its origin from the most primitive species of the subgenus *Cambarus* (*digueti-group*), but developed in a peculiar direction, which is chiefly characterized by the male sexual organs, and by the presence of hooks on the second pereiopods, a condition that is found nowhere else in the genus.

The *distribution* of this subgenus also suggests its antiquity, for it is characterized by a strong discontinuity, *C. shufeldti* being found in Louisiana, the other two species in Mexico. This geographical discontinuity is accompanied by morphological discontinuity, the former species differing very strongly from the two latter. While

C. chapalanus and *montezumæ* still remain in the original home of the genus, although they have changed a good deal, *C. shufeldti* seems to be an early emigrant, which, however, has not much changed. Further investigations in this subgenus are much needed.

Subgenus: FAXONIUS (Type: *C. limosus*).[1]

This subgenus corresponds to Faxon's fourth group, with the addition of *C. pellucidus*. As regards the latter species, which Faxon places with his first group, apparently chiefly on account of the presence of hooks on the third and fourth pereiopods in the male, it is easy to see that the sexual organs do not agree with the *blandingi-type*. Faxon himself says (1885, p. 42), that they are very simple, and generally admits that this species unites characters of different groups. Looking at the figures of the sexual organs given by Hagen (Ill. Cat. Mus. Harvard, 3, 1870, pl. 1, f. 68–71), and Hay (*P. U. S. Mus.*, 16, 1893, pl. 45, f. 11–14), I fail to see any similarity to any of the species of the subgenus *Cambarus*, but their shape approaches rather closely that of some species of Faxon's fourth group, namely: *C. limosus*, *indianansis* and *sloanei*. Indeed, in *C. pellucidus* this organ is different from any one of these, but it agrees with them in the more or less straight and simple form, with the outer and inner parts separated at the tips for a short distance; there is also no trace of a terminal truncation. The rostrum and the chelæ are rather primitive in *C. pellucidus*, while carapace and areola are peculiar, which is possibly a character due to the subterranean life (see Faxon).

If we place *C. pellucidus* with the species of the fourth group named above, it loses its isolated position also with reference to the geographical distribution: it is found in a region (Kentucky and southern Indiana), where at least two of the above species are also found: *C. indianansis* and *sloanei*.

I think, that *C. pellucidus* is a rather primitive form, connecting the subgenus *Faxonius* with the more primitive forms of *Cambarus*

[1] *Astacus limosus* of Rafinesque has been considered by all authors (Girard, Hagen, Faxon) as very probably identical with *A. affinis* of Say. Although Rafinesque's description is very poor, the locality given ("muddy banks of the Delaware near Philadelphia") renders it absolutely certain that *C. affinis* was intended. There is no other species on the banks of the Delaware but this, and it is so abundant there, that it even attracts the attention of the casual observer. Thus I do not see why the older name of Rafinesque should not be restored.

(*digueti-group*), and that the development of an additional pair of hooks on the fourth pereiopods is a parallelism to the similar tendency in the more highly advanced forms of the subgenus *Cambarus* (*blandingi group*) : to the latter, *C. pellucidus* has no direct relation at all.

With regard to all the rest of the species of this subgenus, I agree with Faxon in thinking them to form a natural, genetically connected group. Nevertheless there is much diversity within this subgenus, and is chiefly indicated by the shape of the male sexual organs. Faxon did not use the latter in arranging the species of his fourth group, and thus his key (1885, p. 86) is, as he admits himself, artificial to a degree. But I shall show here, that according to the sexual organs we can divide the subgenus in groups, which seem to be quite natural.

1. *Section : C. limosus.*

Sexual organs short, rather thick up to near the tips, reaching to the base of the third pair of pereiopods. Tips split for a short distance, each tapering to a point. Hooks on third, or on third and fourth pereiopods.

This is the most primitive section of the subgenus, and it is also in other characters quite indifferent, and not highly specialized ; and further, it appears a little heterogeneous. The rostrum is quite uniform in shape, generally with marginal spines (except in certain varieties of *C. pellucidus*), with a rather long or a moderate acumen. The areola is wide and of medium length (except *C. pellucidus*); the chelæ are comparatively narrow and without remarkable features (except in *C. harrisoni*).

The annulus of the female shows the tendency to develop tubercles upon its face ; these tubercles have a more or less central position (*limosus, indianensis*), or a posterior (*sloanei*), or have the shape of a transverse ridge (*harrisoni*), or form a "median keel" (*pellucidus*).

2. *Section : C. propinquus.*

Sexual organs shorter or longer, not thick, deeply split at the tips, tips slender, more or less straight, sometimes the outer one slightly curved, but never both tips curved in the same direction. Always only third pereiopods with hooks (barring freaks).

The other characters are very uniform in this section. The rostrum possesses with one exception (*C. medius*), marginal spines,

and a rather long or moderate acumen. The carapace is of normal shape, oval and depressed; the areola uniformly rather wide, and there is no tendency to become narrow. There are, however, some differences in length: generally, the areola is about half as long as the anterior section of the carapace (incl. rostrum); but in certain species (*erichsoni* and *forceps*) it is slightly, and in one species (*spinosus*) decidedly shorter, and in two others (*rusticus* and *medius*) it is decidedly longer. The chelæ in this section are also rather uniform, but not very primitive: they are more or less broad and ovate. The fingers (in old males) generally are gaping at the base, and in contact distally, and the movable finger possesses a peculiar S-shaped curve. The immovable finger is generally not bearded at the base (a slight indication of a beard is seen in: *C. propinquus*, *obscurus*, *neglectus*). In *C. forceps*, the fingers are unusually and widely gaping, up to the tips. In *C. medius* the chelæ are unusually broadly ovate, and the movable finger has no S-curve.

The annulus of the female is flat, with a median depression and raised margins. Very often the anterior margin is elevated into tubercles, and in *C. hylas* the posterior margin is very prominent, which is rather unusual in this section, and ought to be confirmed by additional investigations.

This section contains ten species, which may be divided into two groups.

1. *Group:* (*propinquus*).

Tips of sexual organs comparatively short, reaching only to the third rarely (*in erichsonianus*) *to the second pereiopods, without or with* (*obscurus*) *a shoulder on the anterior margin. Outer tip regularly tapering from base to end.*

2. *Group:* (*rusticus*).

Tips of sexual organs long, reaching rarely only to the second, generally to the first pereiopods, mostly with a shoulder on the anterior margin. Outer tip not regularly tapering, but thin (*setiform*) *from base to end.*

C. erichsonianus forms a transition between the two groups: the sexual organs are rather long, but they lack a shoulder, and in shape they resemble those of *C. propinquus*.

3. *Section: C. virilis.*

Sexual organs generally quite long (*rarely rather stout*), *reaching about to the second pereiopods, deeply split at the tips, tips slender*

(*rarely shorter*) *and more or less strongly curved backward, both in the same direction. Always only the third pereiopods with hooks* (*barring freaks*).

The shape of the sexual organs is quite uniform in this section, and they do not vary much in the different species, with one exception: *C. difficilis*. Here they are remarkably short and stout, reaching only to the third pereiopods. But we cannot separate this species on this account from the section, since in other characters it is closely allied to *C. palmeri*.

This section closely approaches the *propinquus* type, especially that represented by *C. rusticus*, in fact, the curvature of the tips of the sexual organs is the only important differential character. Besides, however, there is in no case a shoulder developed here, which is so frequently seen in the *propinquus-section*.

In other characters this section is more variable than the *propinquus-section*, and this is most evident in the width and length of the areola. The chelæ are built according to the type of the *propinquus-section*, but a remarkable character is the presence of a dense tuft of hairs (*beard*) at the base of the immovable finger. This beard is absent in *C. compressus* only. In two species, *C. alabamensis* and *compressus*, the chelæ are very broad, and exceptionally smooth.

The annulus of the female is depressed in the middle, with raised margins, similar to that of some species of the *propinquus-section* (*virilis*, *longidigitus*). In other cases it is elevated posteriorly, and the anterior part is depressed; it is never elevated anteriorly, as is generally the case in the *propinquus-section*. (In some species, *alabamensis* and *mississippiensis*, the description of the annulus is inadequate).

The eleven species of this section are easily arranged into three groups according to the areola.

1. *Group*: (*alabamensis*).
   Areola wide and short.
2. *Group*: (*virilis*).
   Areola narrow, of medium length.
3. *Group*: (*palmeri*).
   Areola obliterated in the middle, of medium length.
4. *Section*: *C. lancifer.*
   Sexual organs very peculiar; short, and with slightly curved tips, the outer tip remarkably compressed.

This section is formed to receive an isolated species, the position of which seems quite uncertain. There is a remote resemblance of the sexual organs to those of *C. difficilis* of the third section of this subgenus, and in other characters there are resemblances to *C. mississippiensis*, namely in the lack of marginal spines of the rostrum, and in the obliteration of the areola. The annulus of the female agrees with *C. palmeri* in being depressed in front, and prominent and tuberculated behind: but a similar shape is found in the subgenus *Bartonius*. On the other hand, also the male sexual organs can be compared with *Bartonius*, although they are by no means identical with the very uniform type seen in the latter subgenus. The chelæ, according to the description, are very peculiar, namely long and subcylindrical, the palm with subparallel margins: this is entirely unlike anything that is seen in the *virilis-section* of the present subgenus, and rather stamps this species a primitive one. Then, again, this species presents in the elongate rostrum and antennal scale very unusual features.

Thus it is hard to form a positive opinion about its position. I should not hesitate to place it with the *palmeri-group* of the *virilis-section*, if it was not for the primitive character of the chelæ. According to the latter, and possibly also according to the sexual organs, we might place it at the beginning of the subgenus, as a peculiarly developed primitive form, but it also may be the most highly specialized form of the subgenus. The distribution (Mississippi and northeastern Arkansas) would fit either assumption.

KEY TO THE SPECIES OF THE SUBGENUS FAXONIUS.

1. *Section of C. limosus* (see p. 108).

a_1 Generally third and fourth pereiopods with hooks in the male. Carapace subcylindrical. Areola wide and long. Chelæ subcylindrical. Eyes rudimentary. *C.* (*Faxonius*) *pellucidus* (Tellk.).

a_2 Only third pereiopods with hooks in the male. Carapace ovate, depressed. Areola rather wide, of medium length (about half as long as anterior section of carapace). Chelæ not subcylindrical, compressed, and more or less ovate. Eyes well developed.

b_1 Sexual organs thick, swollen in the middle, tips short and stout, both slightly curved in the same direction. *C.* (*Faxonius*) *harrisoni* Fax.

b_2 Sexual organs short, thick, but not swollen, straight. Tips divergent.

c_1 Sides of carapace with one spine behind the cervical groove.

d_1 Sexual organs with tips not crossed, the outer directed outward, the inner inward. *C.* (*Faxonius*) *sloanei* Bund.

d_2 Sexual organs with tips crossed, the outer directed inward, the inner outward. *C.* (*Faxonius*) *indianensis* Hay.

c_2 Sides of carapace spinose, several spines behind cervical groove, and spines on the hepatical region. Tips of sexual organs crossed. *C.* (*Faxonius*) *limosus* (Raf.).

2. *Section of C. propinquus* (see p. 108).

1. *Group of C. propinquus* (see p. 109).

a_1 Sexual organs reaching to the third pereiopods, with or without shoulder.

b_1 Rostrum with or without median keel. Sexual organs without shoulder on anterior margin. *C.* (*Faxonius*) *propinquus* Gir.

b_2 Rostrum without median keel. Sexual organs with shoulder on anterior margin. *C.* (*Faxonius*) *obscurus* Hag.

a_2 Sexual organs reaching to the second pereiopods, without shoulder. *C.* (*Faxonius*) *erichsonianus* Fax.

2. *Group of C. rusticus* (see p. 109).

a_1 Rostrum with marginal spines. Carapace with a lateral spine.

b_1 Margins of rostrum concave. Sexual organs reaching to the second pereiopods

c_1 Tip and marginal spines of rostrum bent upward. Fingers of chela gaping only at base. *C.* (*Faxonius*) *rusticus* Gir.

c_2 Tip and marginal spines of rostrum not bent upward. Fingers of chela gaping to the tips. *C.* (*Faxonius*) *forceps* Fax.

b_2 Margins of rostrum straight, generally subparallel. Sexual organs reaching to the first pereiopods.

c_1 Rostrum with distinct median keel. Sexual organs without shoulder. *C.* (*Faxonius*) *neglectus* Fax.

c_2 Rostrum without median keel. Sexual organs with more or less distinct shoulder.

d_1 Areola shorter than half of the anterior section of carapace. *C.* (*Faxonius*) *spinosus* Bund.

d_2 Areola half as long as the anterior section of carapace.

e_1 Margins of rostrum almost parallel, *C.* (*Faxonius*) *putnami* Fax.

e_2 Margins of rostrum distinctly convergent. *C.* (*Faxonius*) *hylas* Fax.

a_2 Rostrum without marginal spines. Carapace without lateral spines. *C.* (*Faxonius*) *medius* Fax.

3. *Section of C. virilis* (see p. 109).

1. *Group of C. alabamensis* (see p. 110).

a_1 Areola very short. Carapace not compressed. *C.* (*Faxonius*) *alabamensis* Fax.

a_2 Areola a little longer. Carapace compressed. *C.* (*Faxonius*) *compressus* Fax.

2. *Group of C. virilis* (see p. 110).

a_1 Margins of rostrum concave, acumen moderately long, together with marginal spines bent upward. *C.* (*Faxonius*) *meeki* Fax.

a_2 Margins of rostrum straight, parallel or convergent. Marginal spines and acumen not bent upward.

b_1 Acumen of rostrum long, marginal spines sharp, margins parallel. Fingers of chela long. *C.* (*Faxonius*) *longidigitus* Fax.

b_2 Acumen of rostrum short, marginal spines small or absent, margins more or less convergent.

c_1 Acumen of rostrum not considerably shorter than width of rostrum at base; marginal spines small, but present; margins slightly convergent; upper surface slightly concave. Fingers of chelæ not remarkably long and not emarginate at base.

d_1 Sexual organs longer, slightly curved. *C.* (*Faxonius*) *virilis* Hag.

d_2 Sexual organs shorter, more strongly curved.

e_1 Immovable finger bearded at base, chela for the rest without hairs. *C.* (*Faxonius*) *nais* Fax.

e_2 Immovable finger bearded at base, chela pilose. *C.* (*Faxonius*) *pilosus* Hay.

c_2 Acumen of rostrum considerably shorter than width of rostrum at base; marginal spines generally wanting (rarely present and small); upper surface deeply concave; margins strongly convergent. Movable finger of chela with a deep emargination at base of inner margin. *C.* (*Faxonius*) *immunis* Hag.

3. *Group of C. palmeri* (see p. 110).

a_1 Rostrum with marginal spines.

b_1 Sexual organs long. *C.* (*Faxonius*) *palmeri* Fax.

b_2 Sexual organs remarkably short. *C.* (*Faxonius*) *difficilis* Fax.

a_2 Rostrum without marginal spines. *C.* (*Faxonius*) *mississippiensis* Fax.

4. *Section of C. lancifer* (see p. 110).

Rostrum very long, without marginal spines. Antennal scale very long. Areola obliterated in the middle. Chelæ long, subcylindrical. *C.* (*Faxonius*) *lancifer* Hag.

GEOGRAPHICAL DISTRIBUTION OF THE SUBGENUS FAXONIUS.

The area occupied by this subgenus is almost entirely continuous; it extends over all of the central parts of the United States, from northern Texas to Lake Winnipeg in Canada, and from Kansas to the Appalachian Mountains. To the south, it hardly encroaches upon the domain of the subgenus *Cambarus*, being found only in the northern parts of Alabama and Georgia. To the North, it reaches the Great Lakes, and follows down the St. Lawrence valley. Eastward, the Allegheny Mountains apparently form a boundary, but at two places it has crossed these mountains, namely in the north, where *C. limosus* is found in the lowlands and rivers of

Virginia, Maryland, Pennsylvania and New Jersey; and in the south, where *C. spinosus* and *erichsonianus* cross over from the Tennessee River drainage into that of the gulf and the Atlantic Ocean in Alabama, Georgia, South and North Carolina. These latter cases are continuous, the same species being found in both drainages, while in the former case discontinuity is implied, *C. limosus* being cut off and isolated from the rest of the range of the subgenus.

Generally speaking, this subgenus seems to belong to the great rivers of the interior basin, its center lying about in the region where the rivers Missouri, Mississippi, and Ohio come together, that is to say, in the states of Mississippi, Kentucky, southern Illinois, and southern Indiana. From this center it spreads out in the directions of these rivers and tributaries, chiefly toward the North and Northeast. However, the area remained not restricted to the Mississippi drainage, but crossed the divides into other systems in the following cases: From the Tennessee River two species (*spinosus*, *erichsonianus*) have crossed over into the Gulf and Atlantic drainages, and from the upper Ohio drainage another species (*limosus*) has crossed over into the Chesapeake and Delaware Bay drainage. Another species (*mississippiensis*) is found in the Gulf drainage (outside of that of the Mississippi River) in the state of Mississippi. In the North the area largely extends into the drainages of the great lakes, and even into that of Hudson Bay (through the Red River of the North and Winnipeg Lake).

Studying the distribution of the single sections, the following is to be remarked. The most primitive *section* (that of *C. limosus*) is marked by discontinuity: *C. limosus* being found on the Atlantic coast plain, *C. pellucidus*, *indianensis*, *sloanei* in Kentucky and southern Indiana, *C. harrisoni* in Missouri. This discontinuity, chiefly the isolation of *C. limosus*, is accompanied by morphological isolation, the latter species possessing in its spinosity a character, that only recurs in the allied, but otherwise peculiar species, *C. pellucidus*. This latter species, as well as *C. sloanei*, *indianensis* and *harrisoni*, undoubtedly are the last remnants of the primitive stock of the subgenus in its original home, *i. e.*, in the central basin formed by the three great rivers. Thus the geographical distribution of the *limosus-section* confirms the character of antiquity: most of the species remain in the original

home, while *C. limosus* apparently is an early emigrant that has crossed over into the Atlantic drainage, and has been entirely cut off from the connection with the original stock. At present, I am not prepared to say which was the way by which *C. limosus* reached its present habitat.

The *section of C. propinquus* contains quite a number of species: studying their distribution, we see that the distributional areas of the two groups into which this section is divided correspond to the main ranges of two species, while the other species seem to be rather local forms of these. The typical form of the *propinquus-group*, *C. propinquus*, occupies a continuous range that belongs in part to the Mississippi drainage (Iowa, Illinois, Minnesota), in another part to the Ohio drainage (in Indiana), and for the rest to the Lakes and St. Lawrence drainage (in Michigan, Ohio, Pennsylvania, New York and Canada). Compared with *C. rusticus*, this range is more northern and northeastern, and it is remarkable, that there is hardly a locality known for the typical *C. propinquus*, that lies south of the Terminal Moraine of the Wisconsin ice sheet. *C. obscurus* is found at the eastern edge of the range of *C. propinquus*, namely in the upper Ohio drainage in western Pennsylvania and western New York (See Ortmann, *Ann. Carnegie Mus.*, v. 3, 1905, p. 387–406), and seems to be the representative form of *C. propinquus*, in this region.

C. rusticus, the typical species of the *other group* of this section, has a wide range over the central basin, from Ohio, Indiana, and Kentucky to Iowa, Missouri, and Tennessee. With reference to *C. propinquus* it is more southern and western, although it extends, in Ohio, far northward, and is found in the lake drainage in Michigan and Wisconsin. (The investigation of the distribution of these two species, *rusticus* and *propinquus*, in Ohio, Indiana, Illinois, Michigan, and Wisconsin will certainly be very interesting.) Associated with *C. rusticus* in the same group are six other species: all of these are rather local, and all are found at or near the edge of the range of *C. rusticus*. *C. forceps*, *spinosus*, and *putnami* are found at the southeastern edge, namely in the Cumberland and Tennessee river drainages in Kentucky, Tennessee, and northern Alabama. One of these species (*spinosus*) has crossed over into the Gulf and Atlantic drainages in northern Georgia, South and North Carolina. (This is an additional case throwing light upon

the changes of the drainage systems in the southern Appalachians, see: Simpson, *Science*, 12, 1890, p. 133, and chiefly Adams, *Americ. Natural.*, 35, 1901, p. 844 ff.; where on p. 849 three species of Cambarus are mentioned (*C. spinosus*, *extraneus*, and *erichsonianus*) that belong into this category). The species *C. neglectus*, *hylas*, and *medius* belong to the southwestern and western edge of the range of *rusticus*, and are found in Missouri, Arkansas, Texas, Kansas, and Iowa. Thus it is evident, that the six species morphologically allied with *C. rusticus* in the same group, express this relation also in their distribution, being apparently locally modified forms of the *rusticus*-type, and being naturally found just where we ought to expect them, namely at the edge of the range of this *rusticus*-type.

C. erichsonianus seems to be abnormal: morphologically we have placed it with *C. propinquus*, but its range is far remote from it in eastern Tennessee and central Alabama (in both the Tennessee and Alabama river drainages). But, as we have seen above, its position is a little uncertain, it resembling *C. rusticus* and its allies to a degree, and the distribution suggests the same: it clearly agrees better in this respect with *C. forceps* and *spinosus*, and it would thus become another local form of the *rusticus*-type. Further investigations on this question should be made.

The *third section*, that of *C. virilis*, has been divided into three groups. The *virilis-group* agrees somewhat with the *rusticus-group* in its range, belonging to the central basin, only being a little more western, and considerably more northern: it is hardly found in the drainage of the Ohio, but it is very abundant in that of the Mississippi and Missouri, and crosses over not only into the lake drainage, but also into that of Hudson Bay (Winnipeg Lake). The typical species of the group (*virilis*) occupies almost all of this range, while four other species associated with it (*meeki*, *longidigitus*, *nais*, *pilosus*) apparently are local forms of it, being found at or near the southwestern extremity of the range of *C. virilis* in Arkansas and Kansas. *C. immunis* is a peculiar type of the *virilis-group*, and its range coincides with the southern part of the range of *C. virilis* (Kansas, Missouri, Iowa, Illinois, Indiana, Ohio): this is interesting in so far as this occupation of the same territory by two closely allied species is rendered possible as it seems in this case, by the different habits: as far as we know, *C.*

immunis inhabits the (often temporary) shallow, stagnant ponds and roadside ditches of the western prairies, and is a burrower, while *C. virilis* prefers rocky places in running streams. (See Harris, *Americ. Natural.*, 35, 1901, f. 187 ff., and *Kansas Univ. Quart.*, 9, 1900, pp. 268 and 270).

Of the other two groups of the third section, that of *C. alabamensis* contains only two species, which are very local, being found only in northern Alabama. Both are rather primitive, and apparently are the last remnants in the Tennessee drainage of a once more widely distributed stock. The *difficilis-group* seems to represent a southern extension of the subgenus *Faxonius:* the species are found in western Tennessee, Missouri, Arkansas, Indian Territory, northeastern Texas and Mississippi, all in the drainage of the lower Mississippi (below Cairo), only *C. mississippiensis* belongs to the Tombigbee river drainage.

C. lancifer would agree in its range (Mississippi and Arkansas) with this latter group.

The species of this subgenus, generally, are river-species, and prefer the large rivers of the great central basin. Some species have become lake-forms (*C. propinquus*, for instance), and others ascend the rivers into the smaller streams (chiefly so in the Tennessee and upper Ohio drainages), but they rarely inhabit true mountain streams.

Further investigation of the distribution of this subgenus should pay particular attention to the ways by which several species have crossed the divides of the Hudson Bay, Great Lakes, and Atlantic coast plain drainage systems. It is very likely that wandering of the divides has played here an important part.

Subgenus: BARTONIUS (Type: *C. bartoni*).

This subgenus, which corresponds to the third group of Faxon, is a very natural one, and, in my opinion, contains the most modern and most highly specialized forms in those that have acquired burrowing habits (*diogenes-section*). There are, however, other species, which are rather primitive, as indicated by certain characters.

The length of the areola, in this subgenus, is rather variable: in the *extraneus-section* it is shortest, about half as long as the anterior section of the carapace, and it is even shorter than that in *C. acuminatus*. In all other species it is considerably longer. The an-

nulus of the female is, corresponding to the uniformity of the male organs, also very uniform, and is characterized by its posterior elevation. Aside from the length and width of the areola, the shape of the chelæ, the presence or absence of marginal spines of the rostrum, and the shape of the carapace serve to distinguish the more primitive forms from the more highly developed, and furnish a division of the subgenus into sections as follows:

1. *Section: C. hamulatus.*

Carapace subcylindrical. Rostrum with or without marginal spines. Chelæ long, subcylindrical. Areola rather long. Eyes rudimentary.

Only two species, *C. hamulatus* and *setosus*, belong here, both blind cave-forms. They do not seem to be closely related to one another, since they differ in very important characters. The subcylindrical shape of the chelæ, however, indicates, that both are rather primitive, and have become separated from the primitive stock of this subgenus very early, and probably independently. The shape of the carapace, the long areola, and the rudimentary eyes are very likely due to parallel development, brought about by the similar conditions under which these species are found. (See Faxon, *Pr. U. S. Mus.*, v. 12, 1890, p. 628).

2. *Section: C. extraneus.*

Carapace more or less ovate, depressed, with lateral spines behind cervical groove. Chelæ not very elongated, depressed, and rather broad, but a little more elongated than in the following sections. Areola more or less wide, of medium length, about half as long as anterior section of carapace, sometimes slightly shorter, rarely, in C. cornutus, the areola is rather long. Eyes well developed.

Two of the species belonging here (*C. extraneus* and *jordani*) are typical, and are unquestionably the most primitive forms of the subgenus, as is shown by the shape of the carapace, the rostrum, and chelæ, at least as compared with the following sections. The third species, *C. cornutus*, stands by itself, and is a rather aberrant form, peculiar on account of its antennæ, which have a large, compressed flagellum, ciliated on inner margin. Also the spines of the rostrum (upturned) are peculiar. In the long areola, it is rather advanced. It seems to be a peculiar local form, developed out of the primitive stock now represented by *C. extraneus* and *jordani*, and we may safely leave it with this section, since the only alternative would be to create for it a separate section.

3. *Section: C. bartoni.*

Carapace ovate, depressed, with or mostly without lateral spines. Rostrum without marginal spines. Chelæ comparatively short and broad, depressed, ovate. Areola wide or narrow, generally distinctly longer than half of the anterior section of the carapace, only in one case (C. acuminatus) slightly shorter than half of the anterior section. Eyes well developed.

The four species belonging here are all closely allied to one another. Their chief differences are furnished by the shape of the rostrum, width and length of areola, and shape of chelæ: but all are built according to the same plan.

4. *Section; C. diogenes.*

Carapace ovate, compressed, without lateral spines. Rostrum without marginal spines. Chelæ short and broad, depressed, ovate. Areola very narrow or obliterated in the middle, always distinctly longer than half of the anterior section of the carapace. Eyes well developed.

The five species belonging into this section also form a very natural group. They are connected with the *bartoni-section* through *C. latimanus* (chiefly its var. *striatus* Hay). The peculiar, compressed shape of the carapace (and possibly other characters, as shape of rostrum, narrow areola, shape of chelæ) seems to be closely connected with the habits: all these species (it has *not* been reported for *C. uhleri* but it is likely also the case with this one) are burrowing species and so-called chimney-builders. This habit begins to appear in the *bartoni-section: C. bartoni* often, but not always, makes burrows and chimneys, apparently forced to do so, when the water supply of the small mountain streams, in which it lives, begins to run short in dry seasons. With the species of this group, this habit becomes firmly established, and they never live without making burrows, having abandoned the streams and brooks, and taken to swampy and springy places, generally to the groundwater, where it is found at a short distance below the surface.

The species of this section are distinguishable by the width of the areola, shape of rostrum, shape of the chelæ, and in some cases by peculiar colors. I believe that it is the most highly specialized group of the whole genus, as is indicated partly by the burrowing habits, no doubt an extreme adaptation, and, in one species (*C. uhleri*), by the adaptation to brackish and salt-water, which is found in no other case in the genus.

KEY TO THE SPECIES OF THE SUBGENUS BARTONIUS.

1. *Section of C. hamulatus* (see p. 118).

a_1 Rostrum with marginal spines. Areola wide.
C. (*Bartonius*) *hamulatus* (Cope and Pack.).

a_2 Rostrum without marginal spines (rarely with spines in the young). Areola narrow. *C.* (*Bartonius*) *setosus* Fax.

2. *Section of C. extraneus* (see p. 118).

a_1 Antennæ with normal flagellum.
b_1 Rostrum concave above. Areola rather wide.
C. (*Bartonius*) *extraneus* Hag.
b_2 Rostrum flat above. Areola narrower. *C.* (*Bartonius*) *jordani* Fax.

a_2 Antennæ with very long, compressed flagellum, which is ciliated on the inner side. *C.* (*Bartonius*) *cornutus* Fax.

3. *Section of C. bartoni* (see p. 119).

a_1 Rostrum long, tapering from base to tip. Areola very wide and short, a little shorter than half of the anterior section of carapace. Carapace with lateral spines. *C.* (*Bartonius*) *acuminatus* Fax.

a_2 Rostrum shorter, suddenly contracted to a short acumen. Areola moderately wide or narrow, distinctly longer than half of the anterior section of carapace. Carapace with or without lateral spines.
b_1 Areola rather wide. Chelæ smooth, punctate, inner margin of palm with one or two rows of tubercles.
c_1 Fingers of chelæ broad, slightly gaping at base, not bearded.
C. (*Bartonius*) *bartoni* (F.).
c_2 Fingers of chelæ subcylindrical, widely gaping at base, the outer one bearded at base. *C.* (*Bartonius*) *longulus* Gir.
b_2 Areola narrower. Chelæ rough or tuberculated.
C. (*Bartonius*) *latimanus* (Lec.).

4. *Section of C. diogenes* (see p. 119).

a_1 Areola very narrow, but not obliterated. Color very striking.
b_1 Rostrum broad. Outer margin of hand serrate. Color red.
C. (*Bartonius*) *carolinus* Er.
b_2 Rostrum narrower. Outer margin of hand not serrate. Color blue.
C. (*Bartonius*) *monongalensis* Ortm.

a_2 Areola obliterated in the middle. Color dull, greenish or brownish.
b_1 Rostrum concave above.
c_1 Fingers of chelæ not remarkably flattened, the inner one without distinct excision at base, the outer one not bearded,
C. (*Bartonius*) *diogenes* Gir.
c_2 Fingers of chelæ flattened, the inner one with distinct excision at base, the outer one bearded. *C.* (*Bartonius*) *argillicola* Fax.
b_2 Rostrum flat above. *C.* (*Bartonius*) *uhleri* Fax.

GEOGRAPHICAL DISTRIBUTION OF THE SUBGENUS BARTONIUS.

This subgenus is characteristic for the mountainous regions of the east of the United States, that is to say, for the Appalachian mountains, but the more highly developed, burrowing species have in part descended from the mountains, and spread largely over the central portions of this country. The greatest number of species is found in the southern extremity of the Appalachian system, and there is no question that we have to regard this as the center of origin of the subgenus.

The two cave forms of the *first section* are widely separated from each other. This indicates, on the one hand, that they are not very closely allied, and, on the other hand, the discontinuity thus displayed again indicates antiquity. The one, *C. hamulatus*, is found in a cave in eastern Tennessee, that is to say, right in the center of origin of the subgenus, while the other one, *C. setosus*, comes from a cave in Jasper Co., Missouri (in the Ozark region). This is very remarkable, and very likely indicates, that the center of origin of the subgenus possibly includes the Ozark Mountains, west of the Mississippi: this is further suggested by the reported presence of *C. carolinus* in the northeastern part of Indian Territory, not far from the locality of *C. setosus* (see below). Consequently, we are to regard *C. setosus* as the last remnant of the primitive forms of the subgenus surviving in the western extremity of the original home.

We have regarded, morphologically, the *second section* of the subgenus as the most primitive group of it: this view is supported by the geographical distribution. *C. extraneus* is known from northern Alabama, northern Georgia, Tennessee, and Kentucky (see below, p. 134); *C. jordani* is found in northern Georgia; and *C. cornutus* in Kentucky (locally, only in Edmonson Co.). Thus all the localities are in or near the old center of origin of the subgenus. The presence of *C. extraneus* in the Cumberland and Tennessee river drainages, as well as in the Alabama river drainage indicates an old drainage feature, namely the Appalachian river (see above, p. 116).

The *third section* presents very interesting conditions, such as we have noticed in several groups of the subgenus *Faxonius*. Here we have apparently one widely distributed, typical form, *C. bartoni*: this is found all along the Appalachian mountains and extends very

far to the northeast. This species has followed, in its dispersal, chiefly the direction of the strike of this mountain chain, and reaches now from Tennessee to Maine and New Brunswick. Eastward, it hardly decends to the Atlantic plain, at any rate it does not spread over it, and westward it goes as far as Indiana, always preferring smaller streams in mountainous or hilly regions.

C. bartoni possesses several marked varieties, chiefly at the southern and southwestern extremity of its range, in Kentucky, Tennessee and northern Georgia; one variety (*robustus*) seems to follow the northwestern edge of the range of the main species, from Ohio through northwestern Pennsylvania to western New York (and in Canada). This variety has also been reported from Maryland and Virginia, but I doubt that this is actually the same thing (see below, p. 135).

Besides, there are three other species in this section, which are closely allied to *C. bartoni*. One of them, *C. acuminatus*, is found in North and South Carolina, at the southeastern edge of the range of *C. bartoni;* the second, *C. latimanus*, fringes the southern and southwestern extremity of the area of *C. bartoni* in South Carolina, northern Georgia, northern Alabama, and central Tennessee; and the third, *C. longulus*, is apparently a form belonging to the high mountains, being found in the middle of the southern part of the main range of *C. bartoni* along the highest mountain chains of North Carolina, Tennessee, Virginia, and West Virginia. Thus it is beyond question, that we can regard these three species as local forms of *C. bartoni*, the one belonging to the high mountains, another being its southeastern, the third its southern and southwestern representative.

While the *first* and *second sections* characterize the earlier stage of the distribution of the subgenus, the *third section* expresses its advance and dispersal over the eastern mountain system of the United States.

Finally, the *fourth section* (of *C. diogenes*) offers remarkable conditions. Two of the species, belonging here (*C. carolinus* and *monongalensis*) are evidently a little more primitive than the rest. *C. carolinus* seems to possess a wide range within the Appalachian system. It is a true mountain form, and is found from northern South Carolina to southern Pennsylvania, thus representing the same direction of migration as *C. bartoni*, from southwest to north-

east, parallel to the strike of the mountains. This species, however, has also been reported from Indian Territory (Ozark region). This locality is very strange, and at present is not connected with the main range, no localities being known in Missouri, Arkansas or the larger part of Tennessee (except the eastern extremity). But it is possible that a connection exists here, and if this should be so, this would indicate, as has been said above (p. 121) that the Ozark region is to be included in the original home of the subgenus. *C. monongalensis* apparently is a representative form of *C. carolinus* in southwestern Pennsylvania.

The most puzzling distribution is offered by the remaining three species, of which *C. diogenes* is the most widely distributed. This species has an eastern and a western range on both sides of the Allegheny Mountains. Apparently it has descended from the mountains, that is to say, represents a more highly specialized branch of the original mountain-loving chimney-builders. It has descended into the Atlantic coast plain on the one side, and is found from New Jersey to North Carolina (Cape Fear). On the other side, it has descended westward, and is found from southwestern Pennsylvania over all the states north of the Ohio (also in Kentucky) as far north as Minnesota and Wisconsin, westward to Iowa (also reported from southwestern Wyoming and Colorado), Kansas, and southward to Louisiana. This immense distribution represents possibly the widest known range of any of the species of crayfishes of the United States. The question remains open, whether the eastern and western range of *C. diogenes* is actually connected across the mountains.

Of the other two species, *C. uhleri* clearly is a local form of *C. diogenes*, inhabiting the sea coast (brackish and salt marshes) in Maryland. *C. argillicola* is morphologically very closely allied to *C. diogenes*, and might be regarded, at least in Ohio, Michigan and Canada, as a local form developed at the northern edge of the range of *C. diogenes*. But the fact that *C. argillicola* is also found in central and southern Indiana, in southern Illinois, and that it has been reported from Mississippi and southern Texas (Victoria and Brazoria), does not render this assumption probable: further investigations of the range of these two species (*diogenes* and *argillicola*) in the south and west are desirable, before their mutual geographic relation can be ascertained.

Thus the burrowing species of the *diogenes-section* of the subgenus, while conforming in part to the original habit of living in the mountains, have in another part abandoned their original mountain home, and largely spread over the plains. That this was possible is no doubt due to their peculiar way of living. Aside from *C. gracilis* of the subgenus *Cambarus*, which is also a burrowing form, and occupies a certain part of the western plains, there are no other forms in the central basin that have acquired this habit, and thus *C. diogenes* did not find any competition, and was able to occupy a large territory. That *C. diogenes* is a very vigorous and flourishing form is also demonstrated by the fact that it attains, chiefly on the western plains, a considerable size.

GENERAL CONSIDERATIONS AND CONCLUSIONS.

We have divided the genus *Cambarus* into four subgenera: *Cambarus*, *Cambarellus*, *Faxonius*, *Bartonius*. *Cambarus* originated in Mexico, and immigrated, probably at the beginning of the Tertiary, into the southwestern and southern United States, originally occupying only the southwestern Cretaceous plain, the Ozark Mountains, and the southern extremity of the Appalachian System. A side branch, *Cambarellus*, has also its center in Mexico, and spread, possibly along the sea coast, to Louisiana. In the central and southeastern parts of the United States three new centers developed. The one is a secondary center for the subgenus *Cambarus*, and lies at the foot of the Appalachian Mountains in the lowlands of Alabama and Georgia. Here the more advanced forms of this subgenus took their origin, and spread all over the Atlantic and Gulf coast plain, and further up the Mississippi valley. These are species inhabiting chiefly ponds, lakes, and sluggish streams of the lowlands. Another subgenus, *Faxonius*, developed in the central basin of the three great rivers, spreading over almost all of the Mississippi drainage, and crossing over into the Hudson Bay, Great Lakes, and even into the Atlantic drainages, probably by the aid of shifting divides. The species belonging to this subgenus are chiefly true river species. Finally, a fourth subgenus, *Bartonius*, developed in the mountainous region of the southern Appalachians, probably including also the Ozark region, and from here it spread chiefly over the Appalachian chain in a northeasterly direction as far as New Brunswick. Most of the species belonging

here are inhabitants of smaller mountain streams and brooks. A peculiar group separated from these, the *section of C. diogenes*, which acquired burrowing habits, and is originally also a mountain loving group, but began to descend into the lowlands. Finding no competition here, on account of its peculiar mode of life, it had a chance to spread over a large area.

The centers for the more highly advanced forms of the subgenus *Cambarus*, and for the subgenera *Faxonius* and *Bartonius*, apparently form physiographically differentiated parts of one larger center, situated in the southeast of the United States, clearly corresponding to the southeastern center of dispersal of Adams (*Biological Bulletin*, 3, 1902, p. 115 ff.)[1] Adams discusses this center chiefly with reference to the glacial and postglacial time, but it existed, no doubt, also during the Tertiary, and the development of the different branches of *Cambarus* falls, in my opinion, chiefly into the preglacial time. As Adams maintains, this center is quite distinct from the southwestern center on the arid plateau of Mexico and the adjoining parts of the United States. This latter does not seem to be very important for the later development of the genus, arid regions being generally unfavorable for crayfishes. In older Tertiary times, however, also the southwestern center played a part, in fact it is the original center of the whole genus *Cambarus*.

The different "outlets or highways of dispersal," as Adams (*l. c.*, p. 123) has characterized them, are rather well represented in the distribution of *Cambarus*, and here again I believe, that they were efficient in preglacial times as well as in postglacial times. The Mississippi valley route is represented in the dispersal of the subgenus *Faxonius*, and also by that of the *blandingi-group* of the

[1] Adams' southeastern center does not include the central basin, and he thinks that the Mississippi river (although it undoubtedly possessed a fauna of its own) was largely populated by way of the Tennessee River, which, after having captured the upper course of the old Appalachian River, opened an outlet to its fauna toward the Mississippi. This is no doubt quite correct with reference to the freshwater shells, and, as has been pointed out already by Adams, finds some support in the distribution of certain crayfishes (*l. c.*, p. 849). But as we have seen in the above pages, the center of *Faxonius* in the central Mississippi valley is very marked, and apparently distinct from the other two centers. It is, however, easy to unite all three of them, and regard them as parts of one larger center of older (old Tertiary?) age, including parts that are differentiated physiographically, as indicated above.

subgenus *Cambarus* (*C. blandingi acutus*). The route along the coastal plain seems to be the least frequented, only *C. blandingi typicus* characterizing it. But then again the Appalachian plateau formed a third outlet to the north; this is clearly indicated by the dispersal of the subgenus *Bartonius*. Adams says very pertinently (p. 129): "dispersal is both forward and backward along these highways," and thus we see that in special cases the direction of the migration may become the opposite. In one case (*C. clarki*) we have a reversed current of migration from the southeastern United States toward the southwest, going in a direction opposite to the general direction of immigration of the whole genus. A direction downward the Mississippi valley (southward) is probable in the *palmeri-group* of *Faxonius*, and *C. diogenes* seems to represent the identical reversed direction, descending the Ohio valley from the Allegheny Mountains. The same species shows indications of a reversed migration on the Atlantic coast plain, from Maryland to Virginia.

That the different centers of origin assumed above are very likely correct, is shown by a two-fold consideration. First, the largest number of species of each subgenus is generally found in or near these centers (Adams, *l. c.*, 1902, p. 128: first criterium), and then the more primitive forms of each subgenus are found there (third criterium of Adams). For the subgenus *Cambarus*, this is not entirely true, Mexico possessing only two species, while Kansas possesses three of the more primitive forms, but this may be due to deficiency of our knowledge, or else it is due to interruption and breaking up of the old southwestern range of the genus; it is apparently not so flourishing any more in these parts as it used to be. Of the more highly advanced forms of the subgenus *Cambarus* (*blandingi-section*), the largest number of species is recorded for Georgia (7), Florida (6), and Alabama and Mississippi (4 each). The most primitive forms (*spiculifer-group*) are found in Georgia, Florida and Alabama.

The subgenus *Cambarellus* also makes an exception, two species being found in Mexico, and only one, but this a more primitive one in Louisiana.

The subgenus *Faxonius* possesses the largest number of species in Arkansas (8), and in Missouri and Indiana (7 each). Illinois has only 4, but this may be due to defective knowledge. The more

primitive forms of the *limosus-section* (aside from *C. limosus* itself) are found in Indiana, Kentucky and Missouri, that is to say, in the same general region.

The subgenus *Bartonius* has the largest number of species in Tennessee (6); then follow: Georgia, North Carolina, Virginia and Pennsylvania (with 4 each). The more primitive forms of the *extraneus-section* are found in Georgia, Alabama, Tennessee and Kentucky. In Tennessee is also found one of the blind cave forms (*C. hamulatus*). Thus also here is apparently a mutual relation between center of origin, location of most primitive forms, and center of frequency. This rule, consequently holds good in the section of *C. blandingi* of the subgenus *Cambarus*, and in the subgenera *Faxonius* and *Bartonius*, while it is not very evident in the more primitive forms of the subgenus *Cambarus*, and in the subgenus *Cambarellus*.[1]

A few peculiar and striking facts ought to be mentioned especially.

Discontinuity of distribution proof of antiquity.—We have found this rule substantiated in the following cases: (1) In the distribution of the more primitive forms of the subgenus *Cambarus* (sections of *C. digueti* and *gracilis*); (2) in the subgenus *Cambarellus;* (3) in the *limosus-section* of the subgenus *Faxonius;* (4) in the *hamulatus-section* of the subgenus *Bartonius*. The discontinuity offered by *C. wiegmanni* in the *alleni-group* of the subgenus *Cambarus* needs further investigation, and cannot be regarded as established before the systematic position of this species has been positively ascertained.

Morphologically isolated species occupy isolated stations.—This is illustrated by: (1) *C. cubensis* in Cuba; (2) *C. shufeldti* in Louisiana; (3) *C. limosus* on the Atlantic coast plain from New Jersey to Virginia; (4) *C. harrisoni* in Missouri; (5) *C. alabamensis* and *compressus* in northern Alabama: (6) *C. setosus* in Missouri (cave-form).

Closely allied species occupy neighboring areas. —This is most evi-

[1] Addition to our knowledge may change this considerably. I only call attention to the fact, that up to very shortly ago only two species of *Bartonius* were known from the state of Pennsylvania. Investigations during the last four years have revealed the presence of two more species, thus doubling the number. This may happen in any other state.

dent in the following cases, where groups of species occupy a certain range, but represent each other in the different parts of this range: (1) in the *spiculifer-group* of the subgenus *Cambarus: spiculifer* in northern and central Georgia, *versutus* in central and southern Alabama, and in northwestern Florida, *pubescens* in eastern Georgia, *angustatus* in southeastern Georgia. (2) In the *clarki-group: clarki*, parallel to the Gulf coast from Texas to Florida, *troglodytes* in corresponding localities in Georgia and South Carolina. (3) *Limosus-section* of *Faxonius: indianensis* in southwestern Indiana, *sloanei* in southeastern Indiana and Kentucky. (4) *Propinquus-group: propinquus* has a western and northern distribution; it is represented in western Pennsylvania by *obscurus*. (Between both possibly is *C. propinquus sanborni*, occupying an intermediate range.) (5) *Rusticus-group: spinosus* is southern and eastern (North and South Carolina, northern Georgia, northern Alabama and eastern Tennessee), while *putnami* is more northern (Kentucky). (6) In the *palmeri-group* the different species occupy different parts of a range that includes Mississippi, western Tennessee, Arkansas, Indian Territory and northeastern Texas.

Groups of allied species are often formed by a typical species, which shows a wide range, while the allied species form a fringe on the edge of this range thus representing local forms. This is shown beautifully in the following natural groups: (1) *Rusticus-group:* the typical form is *rusticus*, the local forms at the edge of its range are: *forceps* (southeast), *neglectus* (west and southwest), *spinosus* and *putnami* (southeast), *hylas* (south), *medius* (south); probably also *erichsonianus* (southeast). (2) *Virilis-group:* the typical form is *virilis*, the local forms are: *meeki*, *longidigitus*, *nais*, *pilosus*, all in the southwest. (3) *Bartoni-section: bartoni* is the typical form, the local forms of it are: *acuminatus* (southeast), *latimanus* (south and southwest); in this section also a mountain form has developed within the range (*longulus*), and varieties are found in the southern section of the range, as well as at its northwestern edge. (4) *C. monongalensis* is a local form developed at the northwestern edge of the range of *C. carolinus*. (5) In the *diogenes-section*, at least one species, *C. uhleri*, seems to be a local form of the widely distributed *C. diogenes*, developed at the eastern extremity of its range.

More or less closely allied species, occupying the same or nearly the same territory, generally possess different habits. In most of the

species, we do not know much about their habits, but a few remarkable cases may be mentioned. (1) *C. virilis* and *C. immunis*, although sharply separated, are rather closely allied, and occupy large identical tracts of the central states. We know that *C. virilis* prefers running water with stony bottom, while *C. immunis* is a pond and ditch form (see above, p. 117). (2) *C. monongalensis* inhabits, in western Pennsylvania, almost the same territory that is occupied by *C. diogenes*. The first, however, belongs to the hills, the second to the lowlands (see Ortmann, *Ann. Carnegie Mus.*, v. 3, p. 400).

The various drainage systems have a different effect upon the species of the different subgenera, which is apparently due to fundamental differences in their habits. (1) *Bartonius* is preëminently a mountain-stream group. It goes up into the smallest streams, up to their very sources. In this region, changes of drainage, due to piracy, are common, and rather the rule than the exception, and thus the species quite generally occupy the headwaters of streams running in different directions from the divides. This is exampled by the distribution of the following species: *extraneus*, *bartoni*, *longulus*, *latimanus*, *carolinus*, and probably also by *diogenes*. (See Adams, "Migration of Divides," in *Americ. Natural.*, 35, 1901, p. 844). (2) The *blandingi-section* belongs originally to the lowlands of ths Gulf and Atlantic plain. Here removal of barriers largely has taken place, and thus the species of this group belong to the drainages of different coast rivers, for instance: *lecontei blandingi*, *clarki*, *troglodytes*, *alleni*. (See Adams, *ibid.*, p. 842: "In a country approaching base-level a wide distribution of the fauna will be facilitated.") (3) The subgenus *Faxonius* belongs to the great rivers of the interior basin, and does not ascend far into the headwaters, at least in the mountainous regions, and also does not descend far toward the coastal plain. Consequently, the drainage systems being more permanent, the distribution of these species is more closely connected with the latter. We may, perhaps, compare this — in a very general way — with the period of maximum roughness of Adams (*l. c.*), although this does not hold good for all of this immense region. Indeed, there are important exceptions, and the subgenus has crossed over into the lake-drainage (*C. propinquus*, *obscurus*, *rusticus*, *virilis*, *immunis*), and even into the Hudson Bay drainage (*C. virilis*). This has been brought

about, apparently, by extensive shifting of divides, and we know positively, that this has taken place in great style during and after glacial times. The eastern mountains (Appalachian system) have formed a sharper barrier, but also here certain species have been able to cross: in ancient times *C. limosus*, in more recent times *C. obscurus* (see Ortmann, *Ann. Carn. Mus.*, v. 3, p. 406). The most interesting region is at the southern extremity of the Appalachian system, as we shall presently see.

Very important drainage changes, that have taken place in the southern Appalachian system, are clearly indicated by the distribution of crayfishes, and tend to confirm the results obtained by Simpson and Adams for the freshwater mollusks (see above p. 116). In the region of the Alabama River drainage and that of the Tennessee River, we had at a certain time, a large river running to the South, the Appalachian River, the upper course of which was deflected toward the Northwest, forming the present Tennessee River. The former unity of the drainage system is indicated by identical or closely allied species found now in both systems. The following species illustrate this: *C. erichsonianus*, *extraneus*, *jordani*, *latimanus*, and possibly others. Further investigations of the conditions present in these regions are very desirable.

This is, I think, a rather satisfactory outline-sketch of the distribution of the genus *Cambarus* over the United States. But it is only a sketch, and more detailed investigations are much needed. We see that the migrations of the different groups are very complex, the directions of the migrations crossing at various angles, often being directly opposed to each other. (See map, plate III.)

Further, we are to emphasize, that our knowledge is by no means complete with regard to the distributional facts. There is hardly a single case, where the actual boundaries of a species are known. We have a large number of locality-records, and by plotting them on a map, we obtained a general idea of the range of the different species, but rarely we know the exact limits, and nobody has ever tried to ascertain these, except the present writer in a very limited region, in western Pennsylvania (see *Ann. Carnegie Mus.*, v. 3, 1905). But this ought to be done by all means, and there is no doubt, that very interesting results will be obtained.

It may be remarked in conclusion, that I do not think that a number of reported localities for certain species are trustworthy.

It is astonishing how easy records and museums specimens become mixed up, and a number of localities which are given bona fide by various authors are very questionable. In the following, I put together those records, that appear — at least to me — doubtful or in need of confirmation. At the same time, a number of new records is given which have been made use of in the above pages.

C. blandingi (Harl.).

New Localities. — Millpond at Plainsboro, Middlesex Co., New Jersey, coll. by the writer (Carn. Mus.). — This species is further abundant in the millpond of Grover's Mills, Princeton Junction, Mercer Co., N. J. (seen by the writer), and is rare in the Delaware-Raritan Canal, at Aquæduct near Princeton, Mercer Co., N. J. (seen by the writer).

C. clarki Gir.

New locality. —Devils River, Val Verde Co., Texas, coll. by H. A. Pilsbry, 1903 (specimens in Philadelphia Acad. and Carn. Mus.).

C. limosus (Raf.).

New localities. — Stony Brook, Princeton, Mercer Co., N. J., coll. by the writer, May 30 and Sept., 1898 (Carn. Mus.). — Delaware-Raritan Canal, at Aquæduct near Princeton, Mercer Co., N. J., coll. by the writer, Jan., 1899 (Carn. Mus.). — Delaware River, North Cramer Hill, Camden Co., N. J., coll. by the writer, Sept. 18, 1904 (Carn. Mus.). — Collected by the writer at the following new places in Eastern Pennsylvania in September, 1904: Delaware River, Torresdale Fish Hatchery, Torresdale, Philadelphia Co.; Marcus Hook Creek, Marcus Hook, Delaware Co.; Little Neshaminy Creek, Grenoble, Bucks Co.; Delaware River, New Hope, Bucks Co.; Schuylkill River, West Manayunk, Montgomery Co. (Carn. Mus.). — Further: Tributary of Brandywine Creek, Chadds Ford Junction, Chester Co., Pa. (Acad. Philad.). — Delaware River at Holmesburg, Philadelphia Co., Pa. (Acad. Philad. and Carn. Mus.). — Gettysburg, Adams, Co., Pa., coll. by H. A. Pilsbry (Acad. Philad.). — Potomac River, Cherry Run, Morgan Co., W. Va., coll. by the writer, Sept. 23, 1904 (Carn. Mus.).

Doubtful and spurious older records. — Hagen gives, in 1870, Niagara (L. Agassiz); Lake Erie; New York (Mr. Pike); and Pittsburg. Faxon (1885) drops New York and Pittsburg, but

again gives Niagara (" there is no doubt of the correctness of the determination "), and Lake Erie (Peabody Ac. Sci.). In 1890, Faxon says of the latter specimens, that they " are too small to determine with certainty." He further gives, in 1885, Lake Superior (Boston Soc. Nat. Hist.). I do not entertain the slightest doubt that all these localities are wrong. As to Niagara, which is founded upon the authority of L. Agassiz, we only have to consider that the same locality upon the same authority is given also for *C. propinquus*, and it is quite probable, that specimens of *C. limosus* were put by mistake into a jar containing *C. propinquus*. As to Lake Erie and Lake Superior, some other species may be intended, or a similar mistake has been made: I do not believe, most emphatically, that this species is found in the lake-region. With regard to the absence of *C. limosus* in the state of New York, we possess the testimony of De Kay (Zoöl. N. Y., 6, 1844, p. 23): " I have searched for it (*Astacus affinis*) without success in the tributaries of that stream (Delaware) within the limits of this State."

C. propinquus Gir.

New Localities. — Lake Erie, Lorain Co., Ohio, Lorain gill nets. May 1, 1892, coll. by H. Warden (Mus. Oberlin). These specimens from the lake are the true *C. propinquus*, while all other specimens from the tributaries of the lake in Lorain Co., Ohio, belong to *propinquus sanborni*, see below. Crooked Lake, Oden near Petoskey, Emmet Co., Mich., coll. by E. B. Williamson, Sept. 1, 1904 (Carn. Mus.). This is the northernmost exact locality known, and is very near to a locality recorded by Ward (Bull. Mich. Fish Comm., 6, 1896, p. 15), but not recorded by Faxon, namely: Lake Michigan and Pine Lake at Charlevoix, Charlevoix Co., Mich.

Doubtful Locality. — The latter localities in northern Michigan render it possible that the old records of Lake Superior, given by Hagen on the authority of L. Agassiz, may be correct. But since to L. Agassiz also the record of *C. rusticus* and *virilis* for Lake Superior are attributed, we have again several species mixed up, and it is better to wait for a confirmation.

C. propinquus sanborni Fax.

New Localities. — Oberlin, Lorain Co., Ohio, is the type-locality (Faxon) for this form. I have seen it (Mus. Oberlin) from the

following localities in this region and the state of Ohio: Waterworks reservoir, Oberlin, and Plum Creek, Oberlin; further: Vermillion River, Beaver Creek, French Creek, all in Lorain Co.; Killbuck Creek, Creston, Wayne Co.; Tuscarawas River, Gnadenhutten, Tuscarawas Co. The latter two localities belong to the Ohio drainage, while the rest is lake drainage. This variety forms a morphological link between *C. propinquus typicus* and *C. obscurus*, and seems to be intermediate also in its range.

C. rusticus Gir.

The locality Lake Superior (L. Agassiz) given by Hagen (1870) needs confirmation. As I have shown elsewhere (Ann. Car. Mus., v. 3, 1905, p. 387), the locality Pittsburgh is wrong.

C. neglectus Fax.

New Locality. — Rogers, Benton Co., Arkansas, coll. by H. A. Pilsbry, March 25, 1903 (Acad. Philad. and Carn. Mus.).

C. putnami Fax.

New Locality. — Rockcastle River, Livingston, Rockcastle Co., Ky., coll. by E. B. Williamson, June 21, 1904 (Carn. Mus.). (See Williamson, Ohio Natural., 5, 1905, p. 311.)

C. virilis Hag.

New Locality. — Sandy Lake, Ontario, Canada, coll. by G. H. Clapp (Carn. Mus.). This species has been reported by Ward (Bull. Mich. Fish Comm., 6, 1896, p. 15) from Lake Michigan and Pine Lake, Charlevoix Co., Mich.

The locality Lake Superior, given on the authority of L. Agassiz by Hagen (1870), has been confirmed by Faxon (1885) on the authority of C. L. Herrick, and falls within the known range of the species.

Doubtful Records. — Lake George, N. Y. (L. Agassiz) has been recorded by Faxon (1885) with a ?. It surely is very doubtful.

Faxon also mentions this species from Laramie City in Wyoming; this may be correct, but needs confirmation. He records it further from near Bridgeport, Jackson Co., in northern Alabama, in the Tennessee drainage (U. S. Mus.); I seriously doubt the correctness of this locality, since it is the only one east of the line formed by the Mississippi and Ohio rivers, and is far remote from the rest of the range.

C. immunis Hag.

New Localties. — Lamoni, Decatur Co., Iowa, coll. by J. B. Hatcher (Carn. Mus.). This species is also found in northern

Ohio, as first indicated by Osburn and Williamson (6 Ann. Rep. Ohio Ac. Sci., 1898, p. 21), in Sandusky, Erie, and Lorain Cos., and in Lake Erie. I have seen specimens (Mus. Oberlin) from Huron River, Huron, Erie Co., and from Oberlin, Lorain Co. (Waterworks Reservoir and Plum Creek).

Doubtful Records. — Hagen (1870) gives Huntsville, Madison Co., northern Alabama. This is possibly not this species, at any rate it is "not normal" (Faxon, 1885, p. 100). The locality is too far separated from the rest of the range, to be accepted without hesitation.

Faxon (1885) gives: New York (L. A. Lee); Laramie, Wyoming (U. S. Mus.); Orizaba, Mexico (U. S. Mus.), and further in 1898 he adds: small stream flowing into Oneida Lake, N. Y. The locality in Wyoming may be correct, but we have to try to connect it with the rest of the range, before accepting it. Orizaba, Mexico, is no doubt wrong, and I do not hesitate for a moment to drop it. Oneida Lake in New York seems very strange, since there are no connecting localities with northwestern Ohio. I cannot accept this locality unless verified by unequivocal evidence.

C. palmeri longimanus Fax.

New Locality. — Limestone Gap, Choctaw Mt., Indian Terr., coll. by H. A. Pilsbry (Ac. Philad. and Carn. Mus.).

C. extraneus Hag.

New Locality. — Rockcastle River, Livingston, Rockcastle, Ky., coll. by E. B. Williamson, June 21, 1904 (Carn. Mus.). This is in the Cumberland River drainage; previously, this species was known only from Tennessee, Alabama and Georgia. (See Williamson, Ohio Natural., 5, 1905, p. 310.)

C. bartoni (F.).

New Localities. — Small streams, Princeton, Mercer Co., N. J., coll. by the writer (Carn. Mus.); East Canada Creek, Herkimer Co., N. Y., coll. by R. Ruedemann (Carn. Mus.); Selbysport, Garret Co., Md., coll. by the writer (Carn. Mus.); Cherry Run, Morgan Co., W. Va., coll. by the writer (Carn. Mus.); Greenville, New Castle Co., Del. (Ac. Philad.). The following localities in eastern and central Pennsylvania are represented in the Carnegie Museum (coll. by the writer): Driftwood and Sinnamahoning, Cameron Co.; Keating Summit, Potter Co.; Wills Creek, Mance, Somerset Co.; Cush-Cushion Creek, Indiana Co.; Cresson, Cambria Co.; Ashville, Cambria Co.; Hollidaysburg, Blair Co.;

Wissahickon, Philadelphia Co.; Shoemakersville, Berks Co.; Valley Forge, Chester Co.; Grenoble, Bucks Co.; New Hope, Bucks Co.; West Manayunk, Montgomery Co.; Wallingford, Delaware Co. Other new localities in eastern Pennsylvania are: Headwaters of Loyalsock Creek and Ganoga Lake, Sullivan Co. (Ac. Philad.); Pinegrove, Cumberland Co. (Ac. Philad.).

Doubtful Record. — Lake Superior, given by Hagen on the authority of L. Agassiz, is undoubtedly wrong. As to records of this species from Ohio see *C. bartoni robustus*.

C. bartoni robustus (Hag.).

New Localities. — Small stream tributary to Rockcastle River, Livingston, Rockcastle Co., Ky., coll. by E. B. Williamson, June 21, 1904 (Carn. Mus.). These specimens agree well with young individuals of this variety; adult ones are not in the lot. (See Williamson, Ohio Natural., 5, 1905, p. 310.) Oberlin, Lorain Co., Ohio (Mus. Oberlin). This form was doubtfully reported from Knox Co., Ohio, by Osburn and Williamson (1896). All specimens from Oberlin seen by the writer belong to this variety. The typical form seems to prevail in southern Ohio.

Doubtful Records. — Faxon (1885) gives Decatur, Macon Co., Ill., but this needs confirmation. Further it is doubtful, whether the form called by this name in Maryland and Virginia is identical with the true (northern) *robustus*.

C. bartoni longirostris (Fax.).

Doubtful Record. — Pollard, Escambia Co., Alabama, seems doubtful, since it is close to the Gulf coast, and far away from the original mountain home of this form.

C. latimanus (Lec.).

The locality, Ocean Springs, Miss., is doubtful for the same reason.

C. carolinus Er. (= *dubius* Fax.).

The reported occurrence of this species in Indian Territory (Faxon, 1890) seems strange. It must be looked upon as doubtful till the connection with the rest of the range is established.

C. diogenes Gir.

New localities. — Cooper, Greene Co., Iowa, coll. by J. B. Hatcher (Carn. Mus.); Seaford, Sussex Co., Delaware, coll. by S. N. Rhoads, June 18, 1903 (Ac. Philad. and Carn. Mus.). — Oberlin, Lorain Co., Ohio (Mus. Oberlin). — The specimens from this locality have been mentioned by Osburn and Williamson (1898) as *C. dubius?*, but they are typical *C. diogenes*.

Doubtful records. — Faxon, 1885, gives Deer Park, Garrett Co., Md. This should be confirmed; according to the writer's experience, *C. carolinus* ought to be expected there. If confirmed, this locality will be highly interesting.

Faxon further gives: Cheyenne, Wyoming, and Clear Lake, Colorado; in both cases the most western extremity of the range of the genus is reached. Harris (Kansas Univ. Quart., 9, 1900, p. 267) gives: Boulder, Colorado. This serves to establish the correctness of the above records, but the connection with the rest of the range must be found (I have not been able to locate Clear Lake in Colorado). The southern localities for *C. diogenes* recorded by Faxon, Monticello, Lawrence Co., Miss., and New Orleans, Louisiana, certainly need further support.

C. argillicola Fax.

New locality. — Oberlin, Lorain Co., Ohio (Mus. Oberlin). — I have seen three specimens from Oberlin (adult and young male, adult female), two of which bear the label: Hovey's Ice house, northeast of Oberlin, coll. by Leuthi, Sept. 29, 1892.

Doubtful records. — The localities, Kinston, N. Carolina, and New Orleans, Louisiana, given by Faxon in 1885 are doubtful, as admitted by himself. The localities given in 1898, Victoria and Brazoria, Texas (U. S. Mus.), most emphatically need confirmation.

CARNEGIE MUSEUM,
PITTSBURGH, April 7, 1905.

EXPLANATION OF PLATE VIII.

The plate is introduced to illustrate the *centers of origin*, and the *chief directions of migration* of the different subdivisions of the genus *Cambarus*. Circles or ellipses indicate centers of origin, the lines radiating from these, and ending in an arrow-point, indicate the migration. The different colors mark the different subgenera: *Red, Cambarus; brown, Cambarellus; green, Faxonius; blue, Bartonius.*

It will be remarked that two centers are given for the subgenus *Cambarus*: the one in Mexico marks that of the more primitive forms, the other in Alabama and Georgia, that of the more highly advanced forms (*blandingi-section*). This latter one, as well as the subgenera *Faxonius* and *Bartonius*, took their origin probably from a primitive stock of the subgenus *Cambarus*, immigrated into the southern United States along the broken red line running from Kansas to Alabama.

For further particulars see text, pp. 103, 106, 113, 121, and 124 ff.

Map to illustrate the centers of origin and the chief directions of migration of the different subdivisions of the genus Cambarus.

[Contribution from the John Harrison Laboratory of Chemistry.]

THE USE OF THE ROTATING ANODE AND MERCURY CATHODE IN ELECTRO–ANALYSIS.

BY LILY G. KOLLOCK AND EDGAR F. SMITH.

(*Read April 13, 1905.*)

First Paper.

Several investigations made in this laboratory have shown that when in electro-analysis the anode is rotated high currents can be used and metals be precipitated completely in very short periods of time; further, by the use of mercury cathodes most interesting determinations and separations of metals are possible.[1] In the latter case, however, the anode has been stationary, and the electrolyte consequently not agitated. Then, of course, the precipitation of the metal has been comparatively slow. Observing the splendid results got with the rotating anode, when platinum was the cathode, we determined to use a combination of rotating anode and mercury cathode. This was accordingly done, and in some preliminary trials made last August (1904), the results of which were briefly alluded to in a communication published in the *Jour. Am. Chem. Soc.*, **26**, 1614, mention was made that 0.4810 gram of copper could be precipitated in twenty-five minutes, and that this success could be had with other metals. Since then we have made additional experiments which we desire to record here. Not only is the time factor reduced for the metals studied, but the plan of combining a mercury cathode with the rotating anode gives an inexpensive form of apparatus which will eliminate the platinum dish, cone or cylinder from electro-analysis and thus remove an expensive factor.

Apparatus. — The decomposition cell is a tube 3.5 cm. in diameter and 7.5 cm. in height, made from a test tube. Soften the bottom of the tube in a blast lamp flame, then push through it a platinum wire two centimeters in length, so that its end projects 0.5 cm. into the tube. Flatten the bottom of the tube on an asbestos plate and anneal it in the ordinary way.

[1] *Jour. Am. Chem. Soc.*, **25**, 884: **26**, 1124.

The anode, 7.5 cm. in length, is made from platinum wire 1 mm. in diameter, coiled into a flat spiral 1.5 cm. in diameter. It is inserted in a chuck carried by the rotator which is also provided with three pulleys varying from 2 to 5 cm. in diameter. These pulleys are connected by a belt to two pulleys on the motor. With this arrangement the rotation of the anode could be varied from 100 to 1800 revolutions per minute. During the decomposition an amperemeter, a voltmeter and a rheostat, allowing of resistance from .1 to 100 ohms, were kept in the circuit.

The precautions indicated by Myers in his paper with regard to the decomposition cell were observed. If care be taken to have the cell as clean as possible there will be no trouble experienced with the amalgam subsequently adhering to its sides. The mercury, before using, should be washed with alcohol and ether and after the odor of the latter has disappeared, be placed in the desiccator until it is weighed. It was generally allowed to remain for about five minutes on the balance pan before taking the final weight. In practice a beaker containing a large quantity of mercury, so prepared, should be kept in the desiccator ready for use. The mass of the mercury taken in a single experiment varied from forty to fifty grams. This was frequently used for two or three determinations, except in the case of chromium, where it was found advisable to use it but once. The cathode surface in the first experiments upon zinc was 3.5 sq. cm., but throughout the rest of the work it was about 9 sq. cm. After weighing the decomposition cell and mercury, the solution to be electrolyzed should be introduced. The volume of the electrolyte is always recorded in the accompanying tables. The cell should then be placed upon the copper plate and the anode lowered into the solution. The distance between the cathode and anode depended upon the volume of the electrolyte. When the volume was five cubic centimeters the electrodes were .5 cm. apart and in other instances 1 cm. was their distance apart. The difference did not appear to materially affect the rate of deposition. The tube should be covered. The anode should next be rotated and the connection made with the required number of chloride accumulator cells. The speed of the anode was varied either by using less current for the motor or by changing the combination of pulleys. With the higher currents recorded, the solution was frequently heated to boiling. When this occurred the

current invariably dropped sometimes as much as one ampere. But upon washing down the cover glasses with cold water it rose to its former strength. The dropping of the current is probably due to the accumulation of steam bubbles upon the electrodes. During the electrolysis some of the solution will of course be carried to the sides of the containing vessel and to the cover glasses by the escaping gases or by the agitation of the liquid. After many trials it was found that it is unnecessary to wash down this portion when the higher currents are used. The condensed steam continually frees the sides from the solution. The cover glasses may now and then be tilted against the sides of the tube in order to run off the water which collects in large drops.

It has been repeatedly observed in the present work that the greater the concentration of the electrolyte, the greater the rapidity of deposition, but the last traces of metal were always difficult to remove. For this reason, after a solution had become colorless, the electrolytic action was continued several minutes in order to precipitate the minute amount remaining unprecipitated. It is, therefore, also important to have the volume small toward the end of the decomposition.

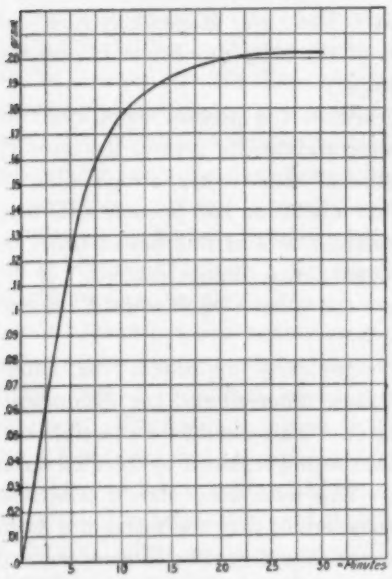
When the metal has been completely deposited, the anode should be stopped, the cover glasses removed and the decomposition cell filled with distilled water. This should then be siphoned off to the level of the spiral and the liquid replaced by distilled water until the current drops to zero. This wash water should always be put aside and tested in order to ascertain that the metal has been completely deposited. The current should next be interrupted and the tube removed and washed again with distilled water, inclining and twirling the cell in order to more completely wash the amalgam. As much of the water as possible should be poured from the cell and the amalgam then be washed twice with absolute alcohol and twice with ether. It should be wiped dry on the outside and after the volatilization of the ether be placed in the desiccator and weighed as previously described.

Experimental Part.

Zinc.

The first experiments made after those described in the *Jour. Amer. Chem. Society* **26**, 1614, were upon zinc sulphate. They

were conducted in order to ascertain the rate of deposition with varying concentration, current strength, electromotive force, speed of anode and how the quantity of metal in the mercury affected the subsequent rate of deposition. The solution for the first experiments contained 0.2025 gram of metallic zinc in 10 cc. This was determined by the electrolytic method, depositing it upon a platinum dish from an ammonium acetate electrolyte. The speed of the anode was 400 revolutions per minute. The current strength was one ampere and the E.M.F. was 5 volts. The volume of the zinc sulphate solution equaled 15 c.c., the current acted thirty minutes. The solution siphoned from the tube showed no trace of zinc. Consecutive experiments so conducted gave the following results in 25 minutes: .2027, .2030, .2025, .2025, .2021, .2027, .2025 grams. Two trials were made with the same conditions but using a volume of 10 c.c. instead of 15 c.c. It was found that the zinc was completely separated in twenty minutes.



CURVE 1. Zinc—1 Ampere, 5 volts.

Experiments were then made to determine the rate of deposition in successive periods of time and the curve constructed from the data thus obtained, using periods of time for abscissas and masses for ordinates. The conditions employed were those given above. The results were as follows:

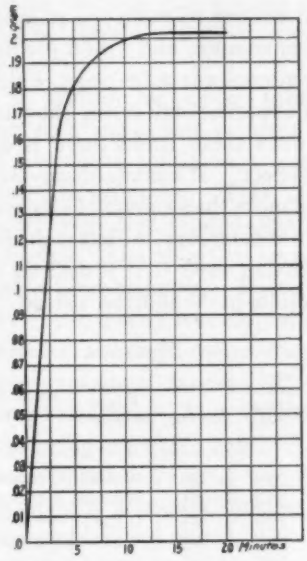
In	5 minutes	0.1196	gram.
"	10 "	0.1774	"
"	15 "	0.1897	"
"	20 "	0.2002	"
"	25 "	0.2027	"

Upon employing a current of 2 amperes, adding sulphuric acid to increase the conductivity, the entire amount was deposited in

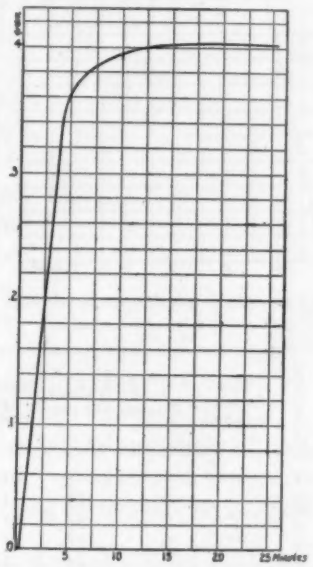
15 minutes. The following conditions were employed: Total volume 15 c.c., sulphuric acid 0.4 c.c., current strength 2 amperes, pressure 7 volts, speed of anode, 500 revolutions per minute.

In	5	minutes	0.1860	gram	of	zinc	was	deposited.
"	10	"	0.1998	"	"	"	"	"
"	15	"	0.2020	"	"	"	"	"

Double the quantity of zinc mentioned above was dissolved in 15 c.c. To this was added .25 c.c. of concentrated sulphuric acid, the anode was rotated at the rate of 800 revolutions per minute and the solution electrolyzed. In thirty minutes the zinc was completely deposited, using a current of 1.5 amperes and 10 volts.



CURVE 2. Zinc —2 Amperes, 7 volts.



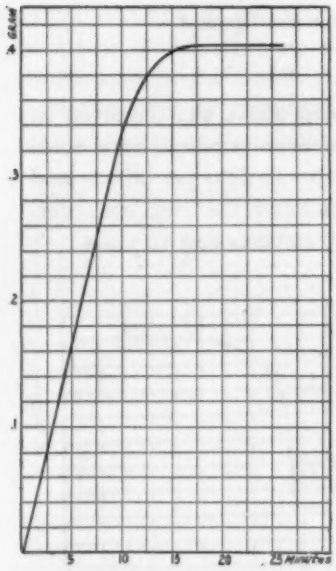
CURVE 3. Zinc–2 Amperes, 6 volts

In	10	minutes	0.3701	gram	was	deposited.		
"	15	"	0.3997	"	"	"		
"	20	"	0.4011	"	"	"		
"	30	"	0.4058	"	"	"		

Curve 3 was drawn from these results.

The same mass of zinc in twenty cubic centimeters was electrolyzed with a current of 2 amperes and 6 volts, other conditions being identical.

In 10 minutes 0.3352 gram was deposited.
" 15 " 0.4010 " " "
" 20 " 0.4030 " " "
" 30 " 0.4050 " " "



CURVE 4. Zinc—1.5 Amperes, 10 volts.

Curve 4 was drawn from these results. A comparison of the third and fourth curves shows the effect of greater dilution upon the quantity of zinc deposited in the first ten minutes.

Two experiments were made to learn the effect of different speeds of the anode upon the rate of precipitation. It was found that the amount of zinc deposited under a rotation of 440 revolutions per minute, and 1,000 revolutions per minute was only .0004, which is within experimental error, showing that between these limits there is no apparent effect. It was also discovered that when more than 1 gram of zinc was present in the mercury, the latter should not be further used if it is desired to obtain results in the shortest period.

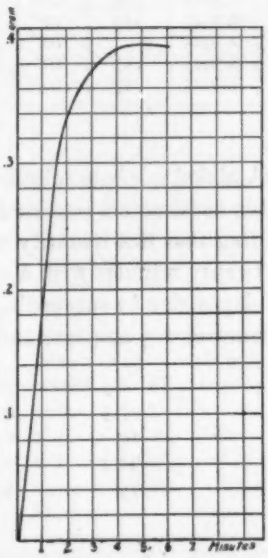
Zinc.

Experiment.	Zinc Present in Gram.	Sulphuric Acid Present in c.c.	Volume in c.c.	Current. Amperes.	Volts.	Revolutions of Anode Per Minute.	Time in Minutes.	Zinc Found in Gram.	Error in Gram.
1	0.2025	0	15	1	7	750	30	0.2027	+0.0002
2	"	0	15	1	7	750	25	0.2030	+0.0005
3	"	0	15	1	7	750	25	0.2015	—0.001
4	"	0	15	1	7	750	25	0.2020	—0.0005
5	"	0	15	1	7	750	25	0.2025	——
6	"	0	10	2	7	750	25	0.2024	—0.0001
7	"	.25	10	2	7	750	30	0.2027	+0.0002
8	0.4050	.25	20	1.5	6	750	45	0.2054	+0.0004
9	0.2025	.25	10	1	5	750	25	0.2025	——
10	"	.25	10	1	5	750	25	0.2029	+0.0004
11	"	.25	15	1	5	750	25	0.2025	——
12	"	.25	15	1	5	750	20	0.2027	+0.0002
13	"	.25	15	2	6	750	15	0.2030	+0.0005
14	"	.25	15	2	6	750	15	0.2020	—0.0005
15	"	.25	15	2	6	750	15	0.2021	—0.0004
16	0.4050	.25	15	5	8	1400	6	0.4057	+0.0007
17	"	.25	15	5	8	480	6	0.4045	—0.0005
18	"	.25	15	5-6	7-5	480	8	0.4042	—0.0008
19	"	.25	10	5	7	640	5	0.4050	——

To 10 c.c. of the zinc sulphate solution 0.4 c.c. of concentrated sulphuric acid was added, after which it was electrolyzed by a current of 5 amperes and 7 volts; the speed of the anode being 640 revolutions per minute. Under these conditions 0.405 gram of zinc was precipitated in five minutes.

COPPER.

Having found that .405 gram of zinc could be deposited in from five to eight minutes it was decided to try other conditions upon copper than those recorded in the previous paper, in order to reduce the time factor. By using higher currents and greater concentration of the electrolyte this was accomplished.



CURVE 5. Copper—5 Amperes, 6 volts.

A solution of copper sulphate containing 0.3945 gram of metallic copper in five cubic centimeters was used for these experiments. This quantity of metal was precipitated finally in five minutes. The solution became colorless in three minutes. Twice this quantity (.789 gram) was deposited in ten minutes, although the solution had become colorless at the expiration of seven minutes. The volume in this case being ten cubic centimeters it appeared the last traces of copper required more time for precipitation. A current of 5 amperes and 6 volts was used, sulphuric acid being introduced to increase the conductivity.

The current strength recorded in the following table was maintained during the greater part of the electrolysis. When it showed a tendency to rise, on the liberation of the acid, additional resistance was thrown into the circuit. The following rates of deposition of copper were determined under the preceding conditions. The anode made 640 revolutions per minute.

In 1	minute	0.1800	gram	of	copper	was	deposited.
" 2	"	0.3400	"	"	"	"	"
" 3	"	0.3664	"	"	"	"	"
" 4	"	0.3945	"	"	"	"	"
" 5	"	0.3945	"	"	"	"	"

Copper.

Experiment.	Copper Present in Gram.	Sulphuric Acid Present in c.c.	Volume in c.c.	Current. Amperes.	Volts.	Revolutions of Anode per Minute.	Time in Minutes.	Copper Found in Gram.	Error in Gram.
1	0.7890	.25	12	3.5	6	1200	10	0.7900	+0.001
2	0.3945	.15	12	4	6	1080	5	0.3941	—0.0004
3	0.3945	.25	12	3.5	6	1200	6	0.3942	—0.0003
4	0.3945	.15	12	5	6.5	1200	5	0.3944	—0.0001
5	0.3945	0	10	2–4	9–7	1200	6	0.3946	+0.0001
6	0.3945	.17	10	3.5	8.5	1200	4	0.3944	—0.0001
7	0.3945	.17	10	4	6	1080	5	0.3946	+0.0001

NICKEL.

A nickel sulphate solution containing 0.4802 gram of metal in ten cubic centimeters was used in the following experiments, and after finding that this quantity was completely deposited in the mercury in twenty minutes with a current of 2 amperes and 7 volts, the rate of deposition in succeeding periods of time was determined with a current of 2.5 amperes and 6 volts.

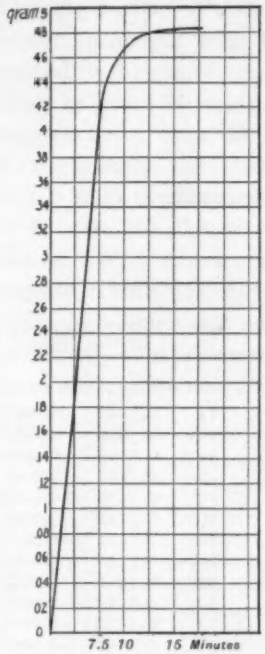
In	2.5	minutes	0.2017	gram of nickel was deposited.				
"	7.5	"	0.4095	"	"	"	"	"
"	10	"	0.4651	"	"	"	"	"
"	12.5	"	0.4774	"	"	"	"	"
"	15	"	0.4802	"	"	"	"	"

Nickel.

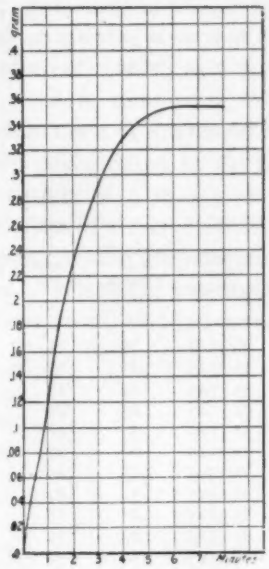
Experiment.	Nickel Present in Gram.	Sulphuric Acid in c.c.	Volume in c.c.	Current. Amperes.	Volts.	Revolutions of Anode per Minute.	Time in Minutes	Nickel Found in Gram.	Error in Gram.
1	0.4802	.25	18	2	7	600	18	0.4802	——
2	0.4802	.25	12	3.5	7	600	16	0.4799	—0.0003
3	0.4802	.25	12	2–4	6.5	600	10	0.4806	+0.0004
4	0.4802	.25	12	6	5	500	7	0.4804	+0.0002
5	0.4802	.25	12	5	6.5	600	10	0.4796	—0.0006
6	0.9604	.25	10–30	4	6	1100	10	0.9597	—0.0007
7	0.4802	.25	12	3	7–5	1100	10	0.4806	+0.0004
8	0.4802	.25	12	3	7	1100	10	0.4796	—0.0006
9	0.9604	.25	12	3.5	7	1100	16	0.9604	——
10	0.4802	.25	12	5	7	640	12	0.4809	+0.0007
11	0.4802	.25	12	5	6	880	8	0.4806	+0.0004
12	0.4802	.25	7	6	5	1200	9	0.4801	—0.0001
13	0.4802	.25	7	6	6	1200	7	0.4801	—0.0001

On employing a current of 6 amperes and a pressure of 5 volts the solution became colorless in four minutes. Not a trace of

nickel was found in the liquid after seven minutes. The amalgam was very bright and of the consistency of soft dough, when one gram of nickel was combined with the usual quantity of mercury (40 grams).



CURVE 6. Nickel—2.5 Amperes, 6 volts.



CURVE 7. Cobalt—5 Amperes, 5 volts.

COBALT.

This metal does not appear to enter the mercury with the same rapidity as nickel under similar conditions. The last minute traces are more difficult to remove. Various conditions were used. When no sulphuric acid was added the current was at first low, but it rapidly rose as the decomposition proceeded. The conditions, giving the total cobalt in the least time, were the following: 10 c.c. of solution, containing 0.3535 gram of cobalt; 0.25 c.c. of sulphuric acid and a current of 5 amperes with a pressure of 6 volts. The speed of the anode was 1,200 revolutions per minute. The solution became colorless in seven minutes, but ten minutes appeared to be necessary for the removal of the last traces of the

metal. On using the same amount of cobalt in a volume of five cubic centimeters, other conditions remaining unchanged, all of the metal separated in seven minutes, thus :

In	1	minute	0.1197	gram.	of	cobalt	was	deposited.
"	3	"	0.2930	"	"	"	"	"
"	5	"	0.3300	"	"	"	"	"
"	6	"	0.3520	"	"	"	"	"
"	7	"	0.3535	"	"	"	"	"
"	10	"	0.3530	"	"	"	"	"

The curve (7) was constructed from these results.

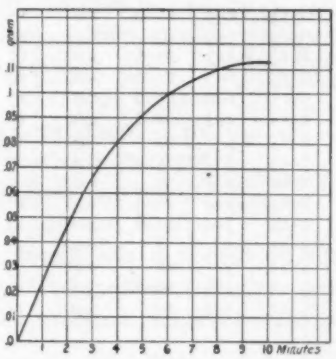
Cobalt.

Experiment.	Cobalt Present in Gram.	Sulphuric Acid Present in c.c.	Volume in c.c.	Current. Amperes.	Volts.	Revolutions of Anode Per Minute.	Time in Minutes.	Cobalt Found in Gram.	Error in Grams.
1	0.3525	.35	15	5	7	1250	15	0.3522	—0.0003
2	0.3525	.25	15	3	5	980	18	0.3524	—0.0001
3	0.3525	.25	15	4	6	600	14	0.3523	—0.0002
4	0.3525	.25	10	4	6	860	16	0.3530	+0.0005
5	0.3525	.5	10	4	6	1000	15	0.3530	+0.0005
6	0.3525	0	10	4	6	1240	16	0.3528	+0.0003
7	0.3525	.25	10	3	6	1200	10	0.3521	—0.0004
8	0.3525	.5	10	6	6	1200	10	0.3530	+0.0005
9	0.3525	.25	10	5	8	800	10	0.3522	—0.0003
10	0 3525	.25	10	3	8	1400	12	0.3523	—0.0002
11	0.3525	.5	10	6	5	800	11	0.3530	+0.0005
12	0.7050	.5	15	6	7	1200	30	0.7052	+0.0002
13	0.1762	.35	10	4	8	560	7	0.1762	——

Chromium.

A solution of chromium sulphate was electrolyzed with currents varying from 1 to 4 amperes and 7 to 12 volts and with a varying quantity of sulphuric acid. It was found by Myers that the addition of the acid was necessary, otherwise, there was a separation of the oxide of chromium throughout the liquid ; but too much acid retards or entirely prevents the decomposition. When 10 drops (40 drops = 1 c.c.) were added and a current of 2.5 amperes and 6 volts applied one half hour was necessary to deposit 0.23 gram of chromium. With 0.5 c.c. of acid and a current of 5 amperes and 4 volts the solution at the end of 60 minutes did not appear to have lost its color. Experiments were then made to learn how

much chromium, if any, was deposited when the acid was present in large quantity. Thus, with a current of 4 amperes and 7 volts, solution containing 1 c.c. of acid, 0.05 gram of metal was precipitated in forty-five minutes; while with two cubic centimeters of acid and a current of 1 ampere and 4 volts the mercury showed no increase in weight after thirty minutes. The following results, obtained in the use of smaller amounts of acid, confirm this. By adding 10 drops of acid (= .25 c.c.) and employing a current of 4 amperes and 7 volts, the liquid became colorless in thirty minutes, but forty minutes were necessary for the complete removal of the metal. With the same quantity of acid, and a current of 5 amperes and 8 volts, the chromium was completely precipitated in thirty minutes. With five drops of acid and a current of 3 to 4.5 amperes and 8 volts, the solution became colorless in eleven minutes. It, therefore, seems that more than three drops of acid are sufficient to materially affect the rate of precipitation. More than two drops of acid must be present to prevent the separation of chromic oxide



CURVE 8. Chromium—3.5 Amperes, 11–10 volts.

which always took place with less than that amount of acid. The following conditions gave the most rapid determination: A volume of the solution, containing 0.1180 gram of chromium and three drops of sulphuric acid (40 drops = 1 c.c.), was electrolyzed with a current of 4 to 5 amperes and six volts, the speed of the anode being 400 revolutions per minute. In four minutes the solution was colorless and in six minutes the chromium was found to be completely deposited. The solution was siphoned off in the man-

ner previously described, but after the cell was removed anhydrous alcohol was poured in as quickly as possible and the operation repeated twice and followed by two washings with ether in order to prevent, if possible, oxidation of the chromium. Oxidation, if it occurred, was but slight, for the error never exceeded 0.0007 gram.

Curve 8 was constructed from the results given below:

In	2	minutes	0.048	gram	of	chromium	was	deposited.
"	4	"	0.085	"	"	"	"	"
"	6	"	0.1000	"	"	"	"	"
"	8	"	0.1105	"	"	"	"	"
"	9	"	0.1185	"	"	"	"	"
"	10	"	0.1185	"	"	"	"	"

Chromium.

Experiment.	Chromium Present in Gram.	Sulphuric Acid. 40 Drops = 1 c.c.	Volume in c.c.	Current Amperes.	Volts.	Revolutions of Anode per Minute.	Time in Minutes.	Chromium Found in Gram.	Error in Gram.
1	0.1180	5	10–15	3–4	7	280	15	0.1186	+0.0006
2	0.1180	3	10–15	2–4	11–9	280	15	0.1187	+0.0007
3	0.1180	3	10–15	1–3	9	640	20	0.1185	+0.0005
4	0.1180	3	8–15	1.5–3	10–8	220	15	0.1186	+0.0006
5	0.1180	3	10–15	1–3	11–9	520	20	0.1186	+0.0006
6	0.1180	3	5–15	1–2	11–9	640	17	0.1175	—0.0005
7	0.1180	3	5–15	2–4	9–8	480	15	0.1180	——
8	0.2360	3	5–15	2.5	10	520	50	0.2355	—0.0005
9	0.1180	5	5–15	3	7.5	400	15	0.1179	—0.0001
10	0.1180	3	7–15	4–5	8	640	6	0.1175	—0.0005
11	0.1180	3	7–15	3–4	10–9	640	10	0.1180	——
12	0.1180	7	7–15	3–4	10–8	200	13	0.1187	+0.0007
13	0.1180	3	5–15	3.5	8	640	11	0.1177	—0.0003
14	0.2360	4	5–15	3	12	640	35	0.2359	—0.0001
15	0.1180	3	5–15	3–4	10–8	320	11	0.1179	—0.0001
16	0.1180	3	5–15	3–4	10	540	11	0.1182	+0.0002

Iron.

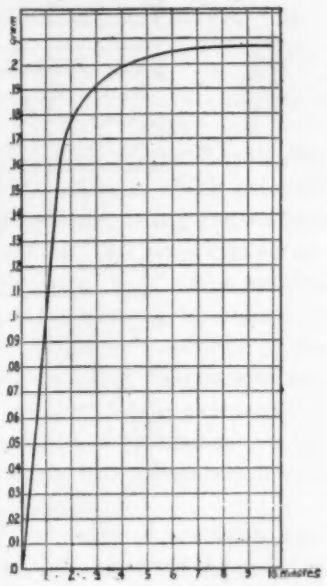
In experimenting with salts of this metal it was soon discovered that sulphuric acid in large amount retarded its precipitation. It was also noticed when higher currents were used that the solution became very hot and assumed a decidedly pink color,[1] which disappeared on the addition of cold water or when the cover glasses were removed, allowing the steam to escape rapidly and thus decreasing the pressure and consequently the temperature of the boiling solution. The color reappeared a few seconds after the cover glasses were replaced.

[1] Due to traces of manganese.

The conditions which gave the most satisfactory results were as follows:

Volume of solution 5 c.c. containing 0.275 gram of metallic iron, 3 drops of concentrated sulphuric acid and a current of 3 to 4 amperes and 7 volts. The rotation of the anode varied from 520–920 revolutions per minute. The iron was completely deposited in seven minutes. The following observations on rate of deposition were made under the conditions just given:

In 2 minutes 0.1760 gram of iron deposited.
" 4 " 0.2000 " " "
" 6 " 0.2050 " " "
" 8 " 0.2075 " " "



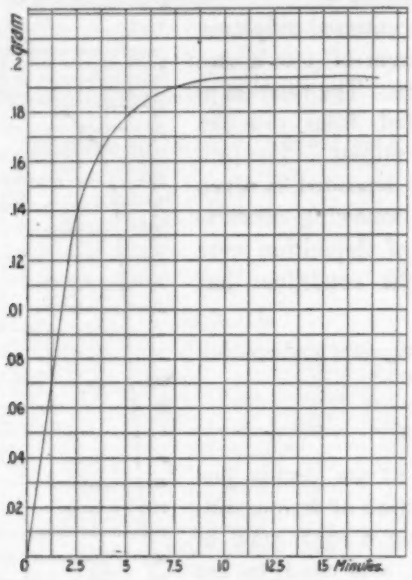
CURVE 9. Iron—3.5 Amperes, 7 volts.

In addition to the results just described a solution of ferrous sulphate containing 0.1945 gram of iron in 10 c.c. was used to get further working conditions. By using a current of 3.5 A. and 10–9 volts, with about 900 revolutions per minute of the anode, the total iron content was deposited in fifteen minutes. The residue from the decompositon cell when oxidized by nitric acid and tested with potassium sulphocyanide gave no color. The

Iron.

Experiment.	Iron Present in Gram.	Sulphuric Acid in Drops. 40 Drops =1 c.c.	Volume in c.c.	Current. Amperes.	Volts.	Revolutions of Anode per Minute.	Time in Minutes.	Iron Found in Gram.	Error in Gram.
1	0.2075	7	5	4–5	8–7	520	14	0.2072	—0.0003
2	0.2075	4	5–15	5–4	6.5–5	680	14	0.2078	+0.0003
3	0.2075	5	5–10	3.2–4	6.5	680	15	0.2077	—0.0003
4	0.2075	3	5	2–2.5	7–6	680	15	0.2073	—0.0002
5	0.2075	3	5	4	6–5	680	10	0.2080	+0.0005
6	0.2075	3	5	3–4.5	7–6	920	7	0.2078	+0.0003
7	0.2075	3	5	2–3	6	740	9	0.2076	+0.0001
8	0.2075	3	5	2–4	6.5–5.5	700	9	0.2076	+0.0001

experiments made to determine the rate of deposition with a lower current (1–2.5 amperes and 10–9 volts) while the other conditions



CURVE 10. Iron—1 to 2.5 Amperes, 10–9 volts.

remained as above, gave the following results which appear in Curve 10.

In	2.5	minutes	0.1141	gram	of	iron	was	deposited.
"	5	"	0.1787	"	"	"	"	"
"	7.5	"	0.1945	"	"	"	"	"
"	10	"	0.1950	"	"	"	"	"

When the residue was tested with potassium sulphocyanide no iron was detected. By the addition of 3 drops (40 drops = 1 c.c.) of sulphuric acid and using a higher current (3.5 amperes) in 10 minutes a faint reaction for iron was observed indicating that the acid has some retarding influence. In fifteen minutes under these conditions the iron had completely separated. By using a higher current 3 amperes and 9 volts under the same condition all the iron was deposited in ten minutes.

UNIVERSITY OF PENNSYLVANIA.

[Contribution from the John Harrison Laboratory of Chemistry.]

OBSERVATIONS ON COLUMBIUM AND TANTALUM.

BY EDGAR F. SMITH.

(*Read April 13, 1905.*)

In 1801 Hatchett, while studying minerals in the British Museum came upon a specimen from Haddam, Conn., which attracted his attention because of its rather high specific gravity and its brilliant black color. A portion of this material was given him for examination, with the result that he discovered in it a new metallic acid, to the metal of which he applied the name columbium. It was his earnest hope that he might obtain larger quantities of the American mineral in order to exhaustively study the new element, and it is of interest to remark that Hatchett fondly expected this material assistance from Thomas Peters Smith, a member of this Society and an enthusiast in chemical science, who on his return from England met an untimely death on shipboard.

In 1802 Ekeberg, of Sweden, while examining an unknown mineral, found that it contained a new metallic acid, to the metal of which acid he assigned the name tantalum, because "when placed in the midst of acids it is incapable of taking any of them up and saturating itself with them." Later, Wollaston (1809) strove to prove that columbium and tantalum were identical. In this he failed. The few reactions known even at that early day differentiated the new elements. About 1840, Heinrich Rose, in studying similar minerals, from other localities, came to the conclusion that the American mineral contained an element absolutely different from tantalum, and called it niobium. Subsequently, owing to his inability to account for the peculiar products which he got by chlorinating a mixture of the oxide of the new element and carbon, he asserted that, in addition to niobium, there was present pelopium (1846). Later (1853), however, he seems to have arrived at the opinion that niobic acid and pelopic acid were different oxides of niobium. The first he called niobic acid and the second hyponiobic acid. Hermann, also, contributed to the uncertainty which surrounded the two elements (columbium of Hat-

chett and tantalum of Ekeberg) in that he announced the existence of ilmenium; but it was not generally accepted by chemists. Hermann, however, persisted in his declaration that it occurred along with the other two elements to which reference has been made. v. Kobell believed that he had detected dianium in allied minerals. This unfortunate state of affairs prevailed until the early sixties, when Marignac, after a careful study of a number of minerals from various localities, announced the existence in them of but two elements — the columbium of Hatchett and the tantalum of Ekeberg — and added that the confusing reactions which had perhaps led Heinrich Rose — but most certainly, Hermann and von Kobell — astray were to be explained by the presence of titanium in all tantalites and columbites. It is only fair to say that Marignac never succeeded in obtaining titanium from any one of the minerals in which, according to him, it occurred, associated together with columbium and tantalum. Indeed, in his concluding paper on columbium he frankly acknowledged that the columbium compounds, which he used for the determination of the atomic weight of the metal, contained titanium, and that he knew of no method by which the latter could be separated from columbium. Marignac's conclusion was accepted by the chemists of the world as final.

When we come to examine the evidence which Marignac gives for the presence of titanium, we find that it is, practically: that the recrystallization of a double fluoride of columbium and potassium, supposed to contain titanium, gave rise, gradually, to a fraction which became more insoluble in water and the molecular weight of its acid oxide approached, within ten or more units, that required by titanic oxide. It is well to bear in mind that at no time did Marignac, whose ability and keen insight one would not for a moment question, give any tests which are ordinarily regarded as indicating titanium. He assumed it to be present on the evidence mentioned above, viz: the greater insolubility of the double fluoride and an approximate molecular weight corresponding to that required by titanic oxide. Ever since Marignac's day chemists the world over have tacitly accepted titanium as associated with columbium in columbites. They have also estimated its quantity by methods suggested from time to time. One of these methods is based on the color reaction which titanium salts give with hydrogen peroxide. Its intensity, compared with that shown

by a known amount of titanium, has been regarded by most analysts as entirely satisfactory. For the determination of the amount of titanium in columbium many methods have been proposed, but this is not the place to discuss them or their value.

As late as 1877, in the last paper published by Hermann, he announced the element neptunium and claimed to have obtained it from the acid mother liquors remaining after tantalum potassium fluoride, ilmenium potassium fluoride and columbium potassium fluoride had been crystallized out. The particular mineral in which he observed it was a columbite from Haddam, Conn.; in other words, the same mineral in which columbium had been originally discovered by Hatchett.

The existence of neptunium has never been contradicted. This is probably because the majority of chemists thought that the verdict in regard to the constitution of tantalites and columbites had been given by Marignac, and that the numerous, unusual reactions of the metallic acids contained in those minerals, noted and commented upon at various times by Heinrich Rose, von Kobell, Blomstrand and Hermann, were all due to the contaminating influence of titanium.

The two elements, columbium and tantalum, in their derivatives, have received comparatively little attention within the last quarter of a century, although at intervals attempts have been made to clear up the mystery which, in a certain sense, surrounds them. In this laboratory, several investigations upon derivatives of them have been made. These being not wholly satisfactory, about three years ago, 50 lbs. of columbite from South Dakota and 25 lbs. from Haddam, Conn., were worked up, with a view of getting an abundant supply of starting-out material; with the view, also, of studying anew the various derivatives of both columbium and tantalum. In the year 1903–1904, Dr. R. D. Hall devoted, in this laboratory, much time and labor to the double fluorides of tantalum and columbium. He made a comparative study of the reactions of the same with the reactions of titanium. His results have been published, but from an examination of them it will be observed that he was not able to find any tests, while using the double fluorides, which differentiated titanium from columbium so thoroughly that he could expect to obtain a complete separation of these two most interesting elements. It is true that he was able, by precipi-

tating potassium columbium fluoride incompletely with ammonia, to get a columbium oxide, which apparently gave no response to the hydrogen peroxide test upon its application, or to the reagent called chromotropic acid. Hence he inferred that he had eliminated the titanium from the columbium. More recent work with large quantities of material has demonstrated that in the latter cases it was impossible to entirely remove the metallic acid which gave the color tests. It was further found that by the action of sulphur monochloride upon the oxides of columbium and titanium, corresponding chlorides were produced; but again, it proved impossible to wholly expel the titanium from the columbium by this process, notwithstanding titanium chloride is an exceedingly volatile liquid and columbium chloride a solid, crystalline body.

In the present year, we have, in this laboratory, prepared large quantities of the double fluoride of tantalum and potassium, and found no difficulty whatsoever in eliminating from it every trace of what was supposed to be the titanium double fluoride.

Having thus, at our disposal, such generous amounts of pure tantalic oxide, free from columbic oxide, in short, really pure tantalic oxide, it was determined to make a new study of the double fluorides of tantalum with the alkali metals and organic bases. This was undertaken in order to discover, if possible, why Dr. Pennington, when working in this laboratory in 1895, obtained double fluorides of tantalum and columbium with cæsium, which showed these unusual formulas: $15CsF.\ TaF_5$ and $7CsF.\ CbF_5$, which varied so widely from those generally followed by the double fluorides of tantalum and columbium, and were not in accord with the law proposed for double halides (*Amer. Chem. Jour.*, v. 291).

At the outstart it was thought that this re-investigation of the double fluorides would prove to be an easy and simple matter. But it was not long until it was seen that the discordant results of Dr. Pennington were probably due to the fact that there was more than one cæsium tantalum fluoride. Indeed, the latest work done in this laboratory, by Mr. C. W. Balke, proves that there are two cæsium tantalum fluorides, two rubidium tantalum fluorides, two sodium tantalum fluorides, two ammonium tantalum fluorides, and so forth, of these ratios:

$TaF_5.CsF$	$2TaF_5.3RbF$
$TaF_5.2CsF$	$TaF_5.2NaF$
$TaF_5.2NH_4F$	$TaF_5.3NaF$
$TaF_5.3NH_4F$	$TaF_5.2KF$

The existence of several such double fluorides with each of the alkali metals naturally raises the question whether these salts ought to be used for the determination of the atomic weight of tantalum, inasmuch as each salt is likely to be contaminated with smaller or larger quantities of the other, depending upon the condition or the care with which they are prepared. Marignac used potassium tantalum fluoride and ammonium tantalum fluoride in his re-determination of the atomic weight of tantalum. It would seem, from the study of the salts just mentioned, that even this skilled and careful analyst could not have been sure that he had a definite, homogeneous body in the determinations which he made. Of course, if there was even a slight amount of a second salt in the salt used for the atomic weight work, it would naturally vitiate the final result. Of all the double fluorides of the alkali metals and bases with tantalum which have thus far been studied by Mr. Balke, that of sodium and tantalum, of the ratio 3 to 2, seems to be the one having some definite and most stable characteristics. We hope to re-determine the atomic weight of tantalum, but it is not probable that we shall use any one of the double fluorides, of which mention has been made, although they appeal strongly because of the ease with which they can be crystallized. The uncertainty, however, as to whether they are really absolutely of one definite ratio every time that they are crystallized is uncertain. Hence they had better be abandoned in atomic weight determinations.

The question may also be asked, may not the double fluorides of columbium with the alkali metals, which have been used for atomic weight purposes, been contaminated with salts of varying ratios? This point will receive attention.

Turning again to columbium, it seems proper to record that having eliminated the tantalum completely from a mixture of oxides obtained from Haddam columbite, the remaining potassium columbium oxy-fluoride was crystallized a number of times from water and also from solutions containing much hydrofluoric acid. This procedure finally gave a mother liquor that was decidedly acid. A metallic acid remained in this mother liquor. According to Her-

mann, in his communication of 1877, this acid should be neptunic acid. Therefore, the acid mother liquor was treated as directed by Hermann; namely, it was evaporated, the residue was dissolved in water and the boiling solution precipitated with an excess of caustic soda. The precipitate, after the liquid had become cold, was filtered out, pressed thoroughly from adherent water and then boiled with 25 times its own weight of pure water. Everything dissolved. The solution was perfectly clear. On cooling, there separated from it the beautiful needle-like crystals of sodium columbate. According to Hermann, the precipitate which was collected, pressed out and then boiled with water, should, if neptunium were present, have left a slimy mass, insoluble in water. This, Hermann said, was sodium neptunate. It should be observed that our experiments were made with the final acid liquors obtained from the double fluorides present in columbite from Haddam; further, that we proceeded in strict accordance with the directions of Hermann and having done all this, did not obtain a gelatinous mass which might have been sodium neptunate. In Hermann's communication, to which reference has been made so frequently, he lays great stress on the fact that the distinguishing reaction of neptunium is the beautiful golden yellow color which sodium neptunate imparts to a salt of phosphorus bead in the *reducing flame*. It is needless to add that we tried on different occasions to find neptunium, according to the directions of Hermann; but our search was fruitless. On one occasion, however, we obtained a mass, not great in amount, which, in the inner blow-pipe flame, did impart a yellow color to the salt of phosphorus bead, but more careful examination of this residue demonstrated that it contained tantalum, iron and some columbium. The intense golden yellow color, which was so strongly emphasized by Herman, we could not get; so that it is very probable that neptunium, like ilmenium and the other metals announced from time to time as present with columbium and tantalum must really be placed in the list of defunct elements. It has not been our wish to bury this candidate for elemental honors. Indeed, we would have been only too glad to have found the evidences of its existence and to have confirmed the observation of that earnest and sincere student of chemical science, who, in his tireless labors, frequently felt confident that he had fallen upon the cause of the varying results observed with columbium and tantalum.

In this connection it may be added that, having freed the tantalum and columbium oxides as thoroughly as possible from ordinary contaminations, the problem of removing tungsten and tin confronted us. After much experimentation, we found that the certainty of the removal of these impurities could only be had by fusing the tantalum and columbium oxides with sodium carbonate and sulphur. It is true that small quantities of tantalum and columbium will be lost, being carried along with the tungsten and tin, but as we were seeking a method of purification and not a separation, we adopted this course. It is the one which was pursued by Heinrich Rose. Our own experience leads us to say that the removal of tungsten and tin from columbium and tantalum oxides cannot be realized by digestion with ammonium sulphide. Indeed, not only did we find the fusion with the sodium carbonate and sulphur necessary, but that working in large quantities of material, as in our case, two and three refusions with these reagents were found necessary. Another point of interest in connection with the purification of the tantalum and columbium oxides may be mentioned. It has frequently been said that in crystallizing out the double fluorides of these metals, if titanium be present with them, it will be found in the potassium tantalum fluoride. We have encountered no difficulty in getting potassium tantalum fluoride perfectly free from what is supposed to be titanium by one or two crystallizations. It has been assumed that as potassium titanium fluoride is rather insoluble in water, it would naturally go with potassium tantalum fluoride. This, however, seems to be an incorrect observation. It masses with the columbium potassium fluoride; at least the element which gives the yellow color with hydrogen peroxide, or a rose red with chromotropic acid is always found associated with the columbium. How to free the columbium from titanic acid we do not know. We are in precisely the same position as that of Marignac, notwithstanding we have probably made greater efforts than he to remove it from the columbium. It is this point in our investigation upon which we have been continuously at work for the last year. We have tried fractional precipitation with ammonia water, fractional crystallization of the double fluorides, fractional chlorination of the oxides in the presence of carbon and the action of numerous organic bases, without finding any way of effecting a separation. Indeed, the separation of columbium and titanium is a problem

which the analyst has not solved up to the present. As remarked, it has received and is receiving our daily attention. Once having achieved this result and having definitely determined the character of the color-giving metallic acid, or proved it to be titanium, without any further doubt, we then hope to subject the purified columbic oxide to a searching review in all its derivatives, just as we are now doing with the compounds of tantalum. In anticipation, it may be said that there are some most interesting complexes of tungstic acid with tantalic oxide and also of tungstic acid and columbic acid. These are under study at present. These complexes, also, have brought analytical problems that are most puzzling. Yet our progress with them leads us to hope for a separation and a satisfactory solution of the same.

Some attention has likewise been given to per-tantalates and per-columbates. It would not be the least surprising to find these derivatives answering admirably for atomic weight work.

UNIVERSITY OF PENNSYLVANIA.

ENQUIRY INTO THE PRESSURE AND RAINFALL CONDITIONS OF THE TRADES-MONSOON AREA.

BY W. L. DALLAS.

(*Read April 14, 1905.*)

In 1900 the writer undertook the discussion of the seven monsoon seasons 1893 to 1899 and showed that during those seven years there occurred a series of oscillations of pressure and that between these oscillations and the monsoon rainfall over India there existed a very distinct and marked relationship. The data used in this discussion consisted of the mean monthly and seasonal variations of pressure over India, derived from all the stations employed in the Daily Weather Report of the Meteorological Department, and the mean monthly and seasonal variations of pressure over the Equatorial Belt and the Arabian Sea as given by the pressure observations recorded (1) at the Seychelles, Zanzibar and Mauritius and (2) on board ships traversing the Arabian Sea and the South-east Trades Region.

The relationship as established for those seven monsoon seasons was as follows: (1) The Indian monsoon rainfall was in defect during the rising portions of these pressure oscillations and in excess during the falling portions while the amount of the rainfall variation agreed directly with the rapidity of the pressure changes. (2) The pressure oscillations exhibited a periodicity of about four years.

It was carefully pointed out at the time that the discussion dealt solely with the seven years under review so that, though the agreement there disclosed was exact and clear, it was obvious that a much longer series of observations would be required before it would be safe to assert that the period of the oscillations and the relationship between the pressure oscillations and the rainfall, as disclosed in the discussions, could be accepted as having a general application. As a matter of fact, before the publication of the paper, it had already become apparent that the relationship had not been maintained, while a simple examination of the existing rainfall data of India showed that there does not obtain any simple

four-year cycle in the Indian rainfall. The author believes that these four-year oscillations form the basis of the weather changes over the Indian monsoon area, though there occur at times violent or spasmodic interruptions, the cause of which is not as yet apparent, and that these interruptions are the cause of the great irregularities in the course of the pressure cycle and in the occurrence of the variations of rainfall. Since the history of these seven monsoon seasons was written, Professor Bigelow's "Contributions to Cosmical Meteorology" [1] has appeared. In it the following paragraph occurs:

"The increase of solar magnetic intensity is synchronous with a diminution of temperature but with an increase of pressure and this function persists throughout every phase of the research. In spite of some irregularity there is a distinct conformity in the general sweep of these curves and also in the tendency to describe crests during the same years. Indeed the occurrence of four subordinate crests in the 11-year periods suggests strongly that a $2\frac{3}{4}$-year period is superposed upon the long sweep of that period curve. Apparently this minor period is the basis of the seasonal variations of the weather conditions of the U. S. A. more than anything else, so that in long range forecasting this period must be very carefully considered."

It will be noticed that the period of these minor oscillations as then determined by Professor Bigelow was $2\frac{3}{4}$ years for the United States. Subsequently Professor Bigelow produced his "Report on the Barometry of the United States" and from the complete data there employed he obtained an eight-year cycle of pressure which is a simple multiple of the four year cycle determined for the Indian Monsoon Area. Professor Bigelow's researches terminate with the year 1899 but where they overlap the Indian series of observations the principal characteristics of the two series agree. Thus Professor Bigelow obtains a maximum in 1896 and a minimum in 1898 with pressure rising again to a maximum through 1899. In the Indian equatorial area the period is approximately four years, and the writer agrees in believing that these minor oscillations of pressure are mainly influential in determining the seasonal variations of weather. On this point it appears probable that the ex-

[1] See Monthly Weather Review, July, 1902, and especially, Weather Bureau Bulletin, No. 21, pp. 125-6, Washington, 1898.

perience of the Indian area will be found to correspond with that of the United States. It must however be born in mind that the investigation is one of extreme complexity and that superposed on the four-year or minor oscillation there are great irregularities which cannot now be explained but which at times completely upset the regular course of the cycle. Notwithstanding these irregularities and interruptions it appeared to the writer that in face of the remarkable agreement between the pressure oscillations and the rainfall during the years 1893 to 1899 it was worth while to continue the discussion in a more exact and detailed manner so as to determine (1) over what area the pressure oscillations extended (2) how far they agreed in amplitude and in time throughout the affected area and (3) what relation the rainfall of the whole monsoon area bore to the pressure oscillations.

The author has collected and discussed a large amount of material and has arrived at certain conclusions which he regards as tentative and far from satisfying. He feels doubtful if the observations would fulfil the requirements which Professor Schuster laid down as a means of estimating the reality of the periodicity, but the investigation has brought out certain relationships which appear at least worthy of record.

The tentative conclusions arrived at are as follows:

(1) That over the trades monsoon area—and most markedly so over the equatorial belt—there occur four-year oscillations of pressure; (2) that during the rising portions of these oscillations the *general* rainfall of the trades monsoon area is below, and during the falling portions is above the average, with a well-marked minimum of rainfall in the first year of the cycle and a well-marked maximum of rainfall in the third year; (3) that from the Antarctic or extreme southern regions there emanate at irregular intervals rays or streamers of varying extent and intensity which occasion increased atmospheric pressure over the affected area; (4) these rays or streamers are apparently not in the least in the nature of waves, as they affect large areas practically simultaneously and continue for considerable periods; (5) when these rays or streamers are frequent and extensive, as in portions of the years 1899 and 1900, pressure ranges largely above the normal, but exhibits large oscillations or fluctuations; when on the contrary they are absent as in portions of the years 1898–1899 pressure is low and the oscil-

lations small; (6) these variations are superposed on the four-year cycle of the tropical belt, and are spasmodic, occurring at irregular intervals over irregular areas so that their influence occasions irregular variations of rainfall and irregularities in the pressure cycles.

There appears to be no satisfactory explanation either of the four-year cycle of pressure over the trades monsoon area or of the irregular spasmodic disturbances of pressure referred to above. With regard to the cycles it is possible that compensatory actions are at work, so that when atmospheric pressure increases in one part of the world it decreases in another, though the evidence of the barometry of the United States is opposed to this and rather suggests that the principal secular variations of pressure are of a uniform character over the whole globe. It is impossible to believe that the variations of pressure are a *result* of variations of rainfall. For one thing, the variations are as marked in a dry area like Aden as in a wet area like Bombay, and for another, the evidence, so far as it can be sifted, shows that the variations of pressure *precede* the variations of rainfall. Thus the increase of pressure which culminated in the large excess of pressure in the months of July, August and September, 1899, commenced in February of that year, thus *preceding* by some months and not *succeeding* the scanty rainfall of that season.

The memoir contains all the figures and data on which the enquiry is founded. Some of the observed changes are at present quite inexplicable, but the observations are given as recorded so that though the author has not succeeded in obtaining any conclusive results, it may be possible for other students of meteorology with more available leisure to work them into a more harmonious scheme.

In order to undertake this detailed examination the employment of pressure or rainfall means of large areas has been abandoned, and instead the actual monthly pressures and their variations for certain selected stations, which it is believed represent fairly adequately the whole monsoon area, have been used. The list of stations includes: Batavia, Calcutta, Bombay, Aden, Cairo, Madras, Colombo, Seychelles, Zanzibar, Mauritius, Durban and Perth, while in addition the marine observations of the Arabian sea and the Equatorial belt have been utilized to obtain averages for those

areas, mainly with the object of determining whether, in the case of these pressure oscillations, there occurs any horizontal translation in the pressure changes or whether they occur simultaneously throughout the whole area.

Numerous tables and figures are given in the memoir to assist in the discussion of the observations.

METEOROLOGICAL OFFICE,
INDIA.

THE RELATION BETWEEN THE ECONOMIC DEPTH OF A BRIDGE TRUSS AND THE DEPTH THAT GIVES GREATEST STIFFNESS.

BY MANSFIELD MERRIMAN.

(*Read April 14, 1905.*)

The fact that there is a certain depth for a bridge truss which renders the quantity of material a minimum has long been known, and the marked increase in the depth of bridge trusses which has occurred during the past quarter of a century is due to the efforts of manufacturers to use the least possible amount of material. It has generally been supposed that the vertical deflection of a bridge under a moving load decreases with the depth, and this is true for plate girders. For a truss, however, investigations made by the author show that the least deflection and hence the greatest stiffness increases up to a certain limit, as the depth increases, and then decreases, so that there is a depth which gives the truss its greatest vertical stiffness.

The following are the results obtained by the author for the type known as the deck Pratt truss. Let l be the span, d the depth, p the panel length, and n the number of panels, so that $l = np$. The economic depth was obtained by forming an algebraic expression for the amount of material in the truss in terms of its dimensions, given loads and allowable unit-stresses, and then finding the value of d/p which renders that expression a minimum. There were found,

for n =	4	8	12	20	30
d/p =	1.29	1.73	2.08	2.65	3.21
d/l =	0.32	0.22	0.17	0.13	0.11

which shows that d/p increases with length of span while d/l decreases with length of span. To determine the depth that gives greatest stiffness, an algebraic expression for the stored energy in the truss due to the deformation of its members was formed and this equated to the deflection due to the given loads. Then the values of d/p that render this expression a minimum were deduced for different values of n, as follows:

for n =	4	8	12	20	30
d/p =	1.29	1.63	1.92	2.38	2.85
d/l =	0.32	0.20	0 16	0.12	0.09

which give laws similar to those of the economic depth, and which show that the depth which gives the greatest stiffness is slightly less than the economic depth. It hence appears that no additional stiffness can be imparted to a bridge by giving to the truss a depth greater than the economic depth.

April, 1905.

ON THE USE OF THE FALLING PLATE OSCILLOGRAPH AS A PHASE METER.

BY WILLIAM McCLELLAN,

RANDAL MORGAN LABORATORY OF PHYSICS, UNIVERSITY OF PENNSYLVANIA.

(*Read April 14, 1905.*)

The wave form of a periodic quantity is the curve which shows the magnitude of the quantity for each instant of time. It is always interesting and careful examination reveals relations that could hardly be discovered in any other way. In alternating current calculations, however, little can be done until the wave form is known accurately. There are two general methods in use, by which it may be determined—the *point to point method* and the *oscillograph* method. In the first, the quantity is measured by a meter, through which the circuit is closed, by a revolving contact-maker, for an instant at any part of the wave for which it may be set. The meter then indicates the value of the quantity at that particular point only. By taking such readings at various points in the cycle, the whole wave may be plotted. As this process is somewhat laborious, various instruments, called *wave tracers*, have been designed to facilitate the operation. In the *Rosa curve tracer* a double potentiometer is used. The operator fixes his eye on the galvanometer, and produces balance by means of a small crank, which turns the cylinder carrying the potentiometer wire. When this occurs, a second lever is pulled, which automatically prints a point of the curve on a paper fixed in the proper position, and also turns the contact-maker to the next position.

Either of the foregoing methods requires considerable time to plot a whole curve. The successive points are obtained from different waves. For example, a good operator can get a curve in five minutes if the instrument is in order. If he is working on a sixty-cycle circuit, he has obtained his curve from 18,000 successive waves. It will be a true curve, therefore, if he has kept his conditions absolutely constant in the interval. This is always troublesome to do, but particularly so in commercial work where the operator seldom has control of the generator. To avoid this

difficulty, the oscillograph has been devised, by which it is possible to obtain the form of a single wave, or a number of successive waves.

The oscillograph is essentially a galvanometer of very short period. The one used in this work as shown in Fig. 1 is of the moving coil type, made under the Duddell patents. The field is

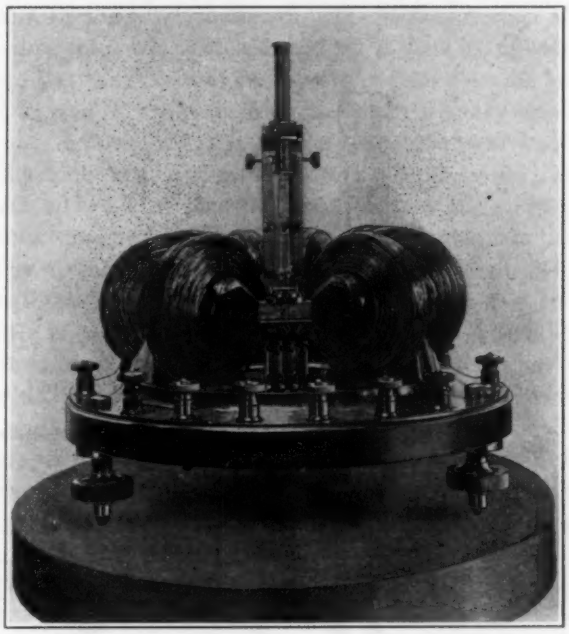


FIG. 1.

supplied by an electromagnet, the coils of which are wound in several sections, so that different voltages may be used for the exciting current. The normal current nearly saturates the core, so that slight changes in the value of the current do not cause appreciable changes in the strength of the field. The coil consists of an inverted U with the ends rigidly fastened at the bottom by a rubber block, and connections made to the binding posts. The upper loop is threaded over a small pulley, to which is fastened the spring by means of which the tension is applied to the strips. There are two distinct loops, thus permitting the taking of two curves simul-

taneously. The free period is approximately one ten-thousandth of a second, undamped. There are three mirrors, one fastened on each coil, and one fixed in the center, to give a zero line. The maximum current used is about one tenth ampere.

To obtain a curve, it is necessary to provide uniform motion perpendicular to the motion of the mirrors. In this instrument it is accomplished by means of a falling photographic plate. This

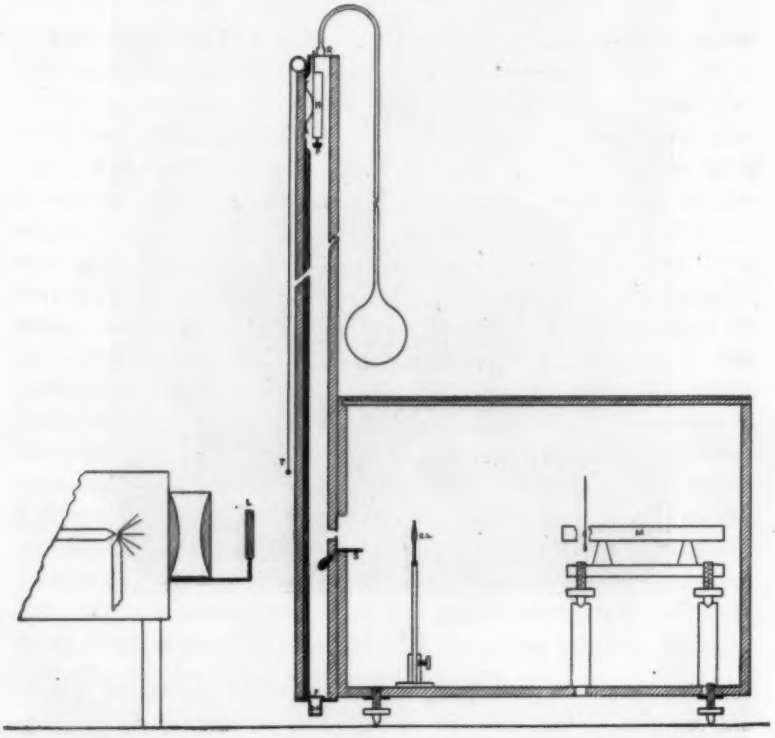


FIG. 2.

motion is uniformly accelerated, but the error in the length of the plate is very slight, though measurable. The error amounts sometimes to about a half per cent. of the wave length. The arrangement can be understood from Fig. 2. The galvanometer *M* is placed in a camera as shown. This is provided with a slit in the end, through which parallel light is sent. The ribbon of light

falls on the three mirrors of the galvanometer, and is reflected to the cylindrical lens *CL*. This renders the parallel ribbon of light a point. The lens is focussed so that this point is in the plane of the photographic plate. The chute through which the plane is dropped is about ninety-five centimeters long, giving the plate a speed which allows the record of one twenty-five cycle wave on a four by five plate. Light enters the chute through a slit which is provided with the hand shutter *S*. The shutter is open when the plate is dropping, but is closed before the plate is pulled back to the top so that the slide may be inserted. This prevents any possibility of fogging. The plate is carried in an ordinary wooden four by five plate holder. This in turn is held by a light wooden carriage *H*, which is provided with springs on the sides and back. These are adjusted so that they just bear on the surfaces of the chute, thus providing a very steady motion of the plate during the fall. The springs also serve the purpose of holding the front of the plate holder tight against the chute. The plate is started by means of a bulb release *R*, and is stopped by an airdash pot *D.P.* The bottom of the carriage is provided with a leather packed brass piston which fits the cup. Light is provided by a powerful 25-ampere arc light, which has the usual condensers. In addition, to get a proper parallel beam, the concave lens *L* is provided. The whole camera is provided with leveling screws, in addition to those for the galvanometer. This is necessary, since the chute must be vertical. The low potential currents used in this work were brought to the galvanometer by lamp cords, which passed through corks in the side of the box. For convenience in lifting the plate holder and carriage the sliding bracket *F* is provided. This is raised by the knob and string *T*, lifting the carriage until it catches in the release apparatus. The bracket then drops to the bottom of the box. It is held in place by a rod, on which it slides. For access to the camera, the whole top of the box is arranged to slide in a light tight groove.

To adjust the apparatus for a curve the chute is first made perpendicular by the outside levelling screws. Then the galvanometer is levelled with its own screws. The arc light is then adjusted so that a strong beam of closely approximate parallel light falls on the mirrors. The galvanometer is then adjusted, if need be, so that the images pass through the center of the slit. Since

the mirrors have practically the same horizontal axis, though they are not in the same vertical plane, necessarily, the spots when focussed on the plate will be in the same horizontal line. They must be adjusted, however, until they have the same vertical axis when not vibrating. This adjustment, as well as the focussing, is done by means of a small glass cylinder with a ground glass end. This is entered through the back of the chute, and is of such a length that the ground glass is in the plane of the falling plate. The focussing is finished and the cylinder removed. After a time, that is with some experience, the focussing can be done from the front of the box. There is no adjustment for the verticality of the mirrors. The coils may be twisted, however, so that they may be brought to various horizontal positions by adjusting screws on the side of the standard.

The double oscillograph permits the simultaneous taking of two independent curves. Since the loops are so fine, and the area of the field so large, comparatively, the loops move in a constant field. The amplitude of the wave is therefore proportional to the maximum value of the current passing through the loops. This will be so only when the damping is critical, that is, sufficient to prevent running past the static position for the same current, and not too much to prevent the loop reaching its static position. A proper adjustment of a non-inductive resistance in series with the loops would make the deflection a definite fraction of an ampere per millimeter. One of the suggested uses to which the double instrument may be put is to obtain the current and potential difference curves for the same piece of apparatus. That this cannot be done, at least exactly, will be apparent from a little study of the conditions. The problem is similar to the wattmeter problem, in which there is always a slight error, due to either the current or the E.M.F. required for one of the coils. The inference is also frequently suggested that the difference in phase, as indicated by the record of the two curves, is the true difference of phase between the quantities. That this is never true, and seldom approximately so, will be apparent from the following discussion :

The simplest method of putting the oscillograph in circuit is shown in Fig. 3. L is the apparatus for which the current and E.M.F. curves are to be determined. O_1 and O_2 are the two loops of the oscillograph joined in circuit as shown. Usually it would be

necessary to have a non-inductive resistance in series with each loop to cut down the current to a proper value. A non-inductive shunt is also frequently used with the current loop. Fig. 4 pro-

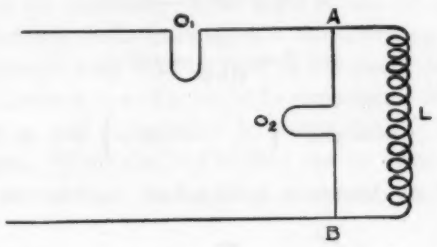


FIG. 3.

vides an analysis of the quantities involved. Let E be the potential difference between A and B. Lagging behind this at an angle α is the current in $L(i)_3$. Also lagging behind E at an angle δ is the current in $O_2(i_2)$. But the current through O_1 is the vector sum of i_2 and i_3 or i_1. Now the angle, or rather the space on the

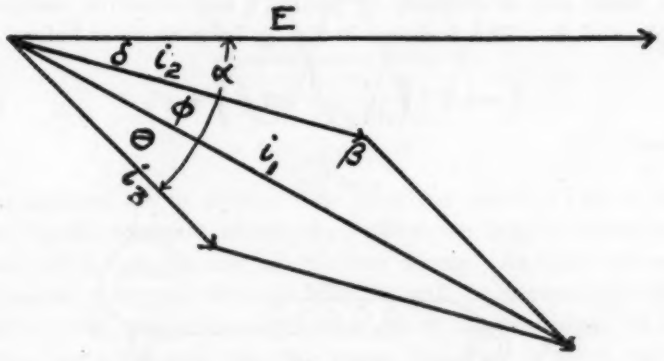


FIG. 4.

plate equivalent to the angle, is of course the angle of phase between i_1 and i_2 and not between E and i_3, as is frequently inferred. It may approach in certain cases, but it is never the true value. The angle desired, that is α, is given by the relation

$$\alpha = \delta + \varphi + \theta. \qquad (1)$$

To obtain it we have the following derivation:

$$\frac{i_1}{i_2} = r = \frac{\sin\beta}{\sin\theta} = \frac{\sin(\varphi+\theta)}{\sin\theta},$$

$$r = \sin\varphi\cot\theta - \cos\varphi,$$

$$\cot\theta = \frac{r}{\sin\varphi} - \cot\varphi,$$

$$\therefore\ a = \cot^{-1}\left(\frac{r}{\sin\varphi} - \cot\varphi\right) + \varphi + \delta. \qquad (2)$$

Before we can determine a, therefore, we have to determine δ.

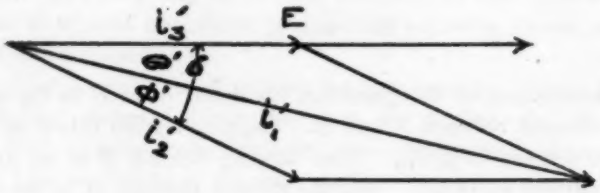


FIG. 5.

The latter may be obtained by putting a non-inductive resistance in place of L. This is shown in Fig. 5, from which as before

$$\delta = \cot^{-1}\left(\frac{r'}{\sin\varphi'} - \cot\varphi'\right) + \varphi', \qquad (3)$$

where

$$r' = \frac{i_1'}{i_2'}.$$

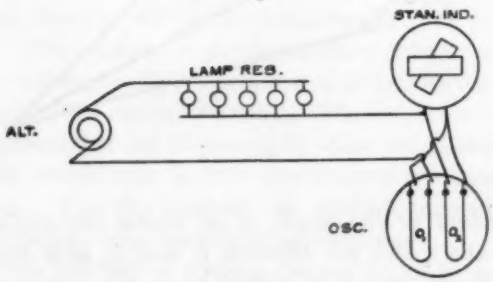


FIG. 6.

To illustrate, and provide a test, arrangements were made as in Fig. 6. An alternator which was under the control of the oper-

ator, so that its speed could be maintained constant, was connected through a lamp resistance, a variable standard of inductance, and the loop O_1, in series. The other loop was connected across the inductance. The resistance of the standard of inductance was 9.89 ohms in all positions. The angle of lag for any given position was therefore easily calculated. Moreover, as the resistance of an oscillograph loop with its fuse, is also about ten ohms, quite a difference between α and φ could be expected. Now we have to determine r, φ, and δ, in order to determine α. The procedure was as follows. With the inductance set to some definite value, L, a plate was taken. Such a plate is shown by Fig. 7. With

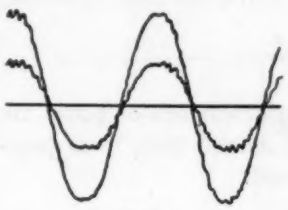


FIG. 7.

FIG. 8.

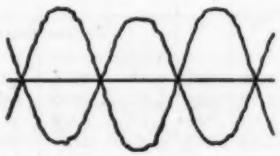


FIG. 9.

the standard set to zero another plate was taken. This is shown in Fig. 8. Now to obtain the ratio r, we have to measure the ratio of the amplitudes of the two waves. As these waves are obtained from two different loops, it will be necessary to obtain the ratio of the galvanometer constants of the two loops. A third plate was taken with the two loops connected in series, and one current passing through both. For accuracy in measurement, the loops were connected oppositely, so that an apparent phase difference of 180 degrees results. This is shown in Fig. 9. The following measurements are then made. $C =$ the ratio of galvanometer constants of the two obtained from ratio of amplitudes in Fig. 9.

$r = i_1/i_2$ obtained from ratio of amplitudes in Fig. 7.

λ_ϕ and $\lambda_{\phi'}$ wave-lengths obtained from Figs. 7 and 8 respectively.

l_ϕ and $l_{\phi'}$ phase displacement, obtained from Figs. 7 and 8 respectively r obtained from ratio of amplitudes in Fig. 7.

During the taking of each plate the value of the frequency must be observed.

R = resistance of the standard of inductance. We then have the following:

$$\varphi = \frac{l_\phi}{\lambda_\phi} 360, \quad \varphi' = \frac{l_{\phi'}}{\lambda_{\phi'}} 360.$$

By substituting φ' and r' in (3) we get δ. By substituting φ, δ and r in (2) we get a. The true value of a is given by the relation

$$a = \tan^{-1} \frac{L\omega}{R}.$$

Values for a as obtained from five different sets of plates are given. A calculation on the first plate showed that δ was practically equal to φ', so that (3) was not used.

No.	C	λ_ϕ	l_ϕ	r	$\lambda_{\phi'}$	$l_{\phi'}$	δ	ϕ degrees.	θ degrees.	a degrees.	L henrys.	$\text{Tan}^{-1}\frac{L\omega}{R}$ degrees.
1	1.14	1.74	.11	1.36	1.76	.025	5.1°	22.8	32.3	59	.040	56.8
2	1.15	1.79	.10	1.55	1.73	.025	5.2	20.0	23.5	47	.030	48.8
3	1.12	1.98	.125	1.36	2.02	.020	3.6	22.3	31.8	59	.040	56.8
4	1.13	2.17	.13	1.36	2.11	.025	4.3	21.6	30.5	57	.040	56.8
5	1.12	2.08	.13	1.37	2.12	.025	4.2	22.3	31.8	59	.040	56.8

$R = 9.89$ $\omega = 377$

It is evident, that in the simplest application of the oscillograph, a mere inspection of the plate is not sufficient to obtain the true difference of phase. The general case is much more complex. This is represented by the diagram of connections in Fig. 10, and the vector diagram in Fig. 11. It is necessary to introduce a series non-inductive resistence in circuit with O_2, and a shunt on O_1, in order to bring the current to a proper size. The letters have the same significance as before, and in addition s is the resistance of the shunt, R' is the series resistance, i_t is the total current, and i_s is the current in the shunt. As before, the angle (Ei_3) is the quantity desired. Now a plate obtained with the connections arranged as in Fig. 10, would give us i_1, i_2, and the angle $(i_1 i_2)$,

granting that the loops have been calibrated so that current values may be measured by them. It is evident that if the multiplying power of the shunt for direct currents is known, i_t can be obtained from i_1 without serious error. Also since s is non-inductive, the angle $(i_1 i_3)$ can be known from a plate taken similarly to Fig. 8. Then the angle $(i_1 i_t)$ can be calculated, and subtracted from the angle $(i_1 i_2)$ leaving the angle $(i_2 i_t)$. Having the latter angle, with i_t and i_2, $(i_t i_3)$ can be calculated, and added to $(i_t i_2)$, and (Ei), which is known as before, thus giving Ei_3, which is the desired angle.

The writer has not worked the latter discussion out for two reasons. First, the errors of measurement on a photographic plate

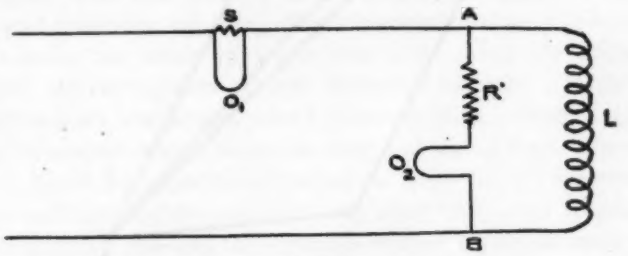


FIG. 10.

would not permit of any accurate results since in any case the angles are small. Second, in the large majority of cases, the multiplying power of the shunt is so large, that the currents i_1 and i are in the same phase, so far as could be measured. Also the resistance in the O_2 circuit so large that E and i are in the same phase. Therefore the angle desired can be obtained exactly as δ was in the preceding discussion, with the introduction of the multiplying power of the shunt. The use of ammeters in some of the circuits would greatly facilitate matters in many cases.

The above discussion shows that, with the oscillograph, the phase angle can be calculated. In no case can it be obtained by a simple measurement on a single plate. Owing to the thickness of the lines traced by the moving spot, measurements cannot be made closer than a quarter of a millimeter, so that a long curve must be obtained if any accuracy is to be attained, especially with small differences of phase. While the double oscillograph could not be recommended in any way as a phase meter, yet it does permit an ap-

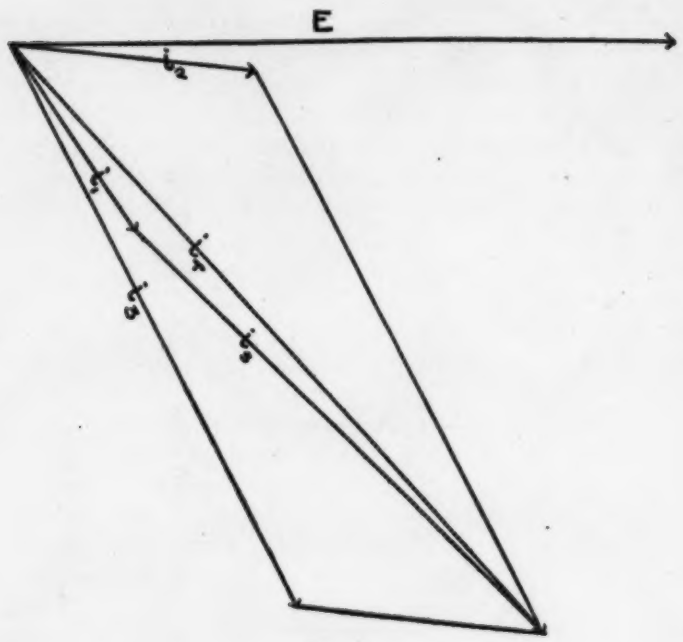


FIG. 11.

proximate value of this quantity being obtained. In most of the cases to which the instrument has been applied, the process would be quite simple, owing to the magnitude of the quantities involved. The fact that the angle can be obtained is valuable in those cases where curves are taken under fleeting or unknown conditions, in which other methods could not be applied.

[Contribution from the John Harrison Laboratory of Chemistry.]

SOME OBSERVATIONS ON COLUMBIUM.

BY ROY D. HALL AND EDGAR F. SMITH.

(*Read May 19, 1905.*)

The starting-out material in this study was columbite from Lawrence County, South Dakota. Its specific gravity equaled 5.86. It contained 81 per cent. of the mixed oxides of columbium and tantalum. The total quantity of substance decomposed by fusion with acid potassium sulphate (58.5 kilograms) was 21.3 kilograms. Each fusion was made in a platinum dish, using 100 grams of mineral and 275 grams of acid potassium sulphate. While still liquid the mass was poured into a porcelain dish. When cold the fusion separated readily from the dish and was broken into small pieces, which were boiled with water in large No. 11 evaporating dishes until thoroughly disintegrated; when they were transferred to precipitating jars and the hydrates washed by decantation until the wash water gave no precipitate or only a slight precipitate with ammonium hydroxide. The solution and the washings were evaporated to dryness. The residue was designated part I. The moist hydrates of columbium and tantalum were covered with ammonium sulphide and allowed to stand for several days. This ammonium sulphide solution was decanted and designated part II. The remaining oxides were finally treated with very dilute sulphuric acid and then thoroughly washed with water. The washings and the diluted sulphuric acid solution were also evaporated to dryness and marked part III. The residue labeled part I contained potassium and the bases from the mineral in the form of sulphates. It was dissolved in water, poured into five-gallon jars and there precipitated with a slight excess of ammonium hydroxide. Having decanted the supernatant liquid the precipitate was washed once with water, after which the hydrates were covered with a solution of ammonium carbonate and allowed to stand for several days. The ammonium carbonate solution was then siphoned off, acidulated with dilute hydrochloric acid, and any metal present precipitated

with a slight excess of ammonium hydroxide. The hydrate obtained in this way was dissolved in dilute hydrochloric acid, and an excess of ammonium carbonate, together with ammonium sulphide, added to its solution. The iron separated in the form of sulphide and with it there was a small amount of titanium. The filtrate from this precipitate was boiled with hydrochloric acid and ammonium hydroxide added. The hydrate which was precipitated was ignited and tested as to its photographic power. It gave a picture after an exposure of five days. It contained uranium. It showed the greenish color characteristic of U_3O_8. After this it was fused with acid potassium sulphate, taken up in water and the solution boiled. A precipitate formed on cooling but disappeared on warming, thus indicating the presence of members of the cerium group or of zirconium. On the addition of ammonium hydrate there separated a hydrate which, after filtration and washing, dissolved completely in a solution of oxalic acid. This pointed to the presence of zirconium. The hydrates were again precipitated, dissolved in sulphuric acid, and the solution neutralized with potassium carbonate and saturated in the cold with potassium sulphate. By this precipitation the zirconium was obtained in the form of insoluble double sulphate, while the uranium remained in solution. After filtering out the zirconium potassium sulphate it was dissolved in hydrochloric acid and zirconium hydrate precipitated with ammonium hydroxide. It was well washed with water and dissolved in hydrofluoric acid. An equivalent amount of potassium carbonate was added and, on evaporation, potassium zirconium fluoride crystallized out. Three grams of this salt were obtained.

Analysis. — 0.5043 gram of the salt ignited with sulphuric acid gave 0.5272 gram of $K_2SO_4 + ZrO_2$, and contained 0.2212 gram of ZrO_2, leaving 0.3060 gram of K_2SO_4.

	Calculated K_2ZrF_6.	Found.
$2KF$	41.05	40.47
ZrF_4	58.95	59.52
	100.00	99.99

The uranium in the filtrate from the zirconium was precipitated with ammonium hydroxide, dissolved in hydrochloric acid, and an excess of sodium hydroxide added to this to obtain the glucinum. This was not found. The uranium was changed to nitrate and the

solution allowed to evaporate, when large characteristic crystals of uranium nitrate separated. The solution decanted from the original ammonium hydroxide precipitate, which contained manganese and allied elements, was treated with an excess of sodium carbonate. The precipitate produced was allowed to settle, the supernatant liquid decanted into other jars, and hydrogen sulphide passed through it. A small amount of a black sulphide was obtained. It consisted of zinc, iron, copper and nickel (from the crucible tongs). The precipitate produced by sodium carbonate contained manganese, zinc and iron. Ten grams of it were dissolved in hydrochloric acid and the iron removed by the basic acetate method. The zinc was then precipitated as sulphide. The latter was changed to chloride and tested for gallium. Not a trace of the latter was found. Zinc lines alone were shown in the spectrum.

Tin and tungsten were contained in part II. Part III was not further examined. It may be concluded, therefore, that the columbite from South Dakota contains as acids: tantalum, columbium, titanium, silicon, zirconium, tin and tungsten; as bases: iron, maganese, zinc, uranium, copper (?) and nickel (?).

The moist metallic acids, after having been washed with dilute sulphuric acid, were brought into a large platinum dish and dissolved in fairly concentrated hydrofluoric acid. This solution was then filtered, through a hot water funnel, from undecomposed mineral and from potassium silicofluoride (due to the presence of some potassium sulphate in the moist oxides). The hydrofluoric acid solutions were collected in large rubber dishes and sufficient potassium hydroxide was introduced to convert the tantalum into potassium tantalum fluoride, most of which separated out and was removed by filtration. This precipitate was dried as far as possible by suction. It was washed once and then allowed to dry in the air. It weighed 11 kilograms. The mother-liquor from the potassium tantalum fluoride was evaporated in stages, potassium hydrate being added. The columbium separated usually in hexagonal, hard, short crystals, such as separate from a strongly acid solution containing an insufficient amount of potassium fluoride. The total residue obtained in this way amounted to about 8 to 10 kilograms. These residues were decomposed by treating them with twice their own weight of sulphuric acid, heating gently until the bulk of the hydrofluoric acid was expelled, and then evaporating

until the mass fumed strongly and maintaining the temperature until the excess of sulphuric acid had been almost completely driven out. Several hours were required for this. It is necessary in order to get rid of the hydrofluoric acid. The residual mass was boiled with water to extract the bases which dissolved as sulphates. The insoluble hydroxides were thoroughly washed and dissolved in hydrofluoric acid. The first crop of crystals, obtained by evaporation with potassium hydroxide, was removed and the mother-liquor then evaporated to dryness with sufficient potassium hydroxide to change all of the metallic acids into double fluorides. A portion of these crystals (first crop) was dissolved in water and the tantalum removed by adding dilute potassium hydroxide to the solution, which, after the formation of a permanent precipitate, was boiled for some time. The precipitate consisted mainly of potassium tantalum oxyfluoride. It was filtered out and the filtrate evaporated to dryness. The residue was baked for some time at 200°. By this procedure some hydrofluoric acid was expelled and, on taking up the residue with water and boiling, more potassium tantalum oxyfluoride separated. By repetition of this process all of the tantalum was removed from the solution. The only test relied upon for the detection of tantalum was the solution of this precipitate in a drop of hydrofluoric acid and evaporation to crystallization. If needles separated their solubility in water was used to ascertain whether they were potassium tantalum fluoride or potassium columbium oxyfluoride. It is true that this test consumes considerable time, yet it is the only satisfactory means of determining with which of the metals the chemist is dealing. The formation of a precipitate by protracted boiling of a dilute solution of potassium tantalum fluoride is not conclusive, for Krüss and Nilson (Ber. 1881, 1676) have shown that potassium columbium oxyfluoride deposits under like conditions a small amount of a salt containing less fluorine. Further, the double fluoride must be recrystallized several times, so that it will be sufficiently free from acid that tantalum, if it is present in small amounts, may be precipitated by boiling.

Having freed the double fluoride from tantalum it was dissolved in water and hydrogen sulphide conducted through its solution. A slight precipitate of platinum sulphide was obtained. The filtrate from it was evaporated to dryness and the residue baked.

On dissolving in water more platinum sulphide was found, but when hydrogen sulphide was conducted through the filtrate no further precipitation took place. The first crop of crystals got by the evaporation of this solution showed the usual form of potassium columbium oxyfluoride. They were allowed to dry in the air and labeled crystals No. 1 (A). The filtrate from them was reduced to a small bulk. Strong hydrofluoric acid was added when the needles of potassium columbium fluoride (K_2CbF_7) separated. These were dried between bibulous paper and labeled crystals No. 2 (B). Samples from these two crops of crystals were analyzed.

Analysis of No. 1 (A):

0.53 gram of salt gave 0.2346 gram of oxide and
0.3161 gram of potassium sulphate

$0.2346 : 0.3161 :: x/2 : 174 \qquad x = R_2O_5 = 258.2.$

	Calculated. $K_2CbOF_3H_2O$.	Found.
K_2SO_4	57.81	59.64
Oxide	44.52	44.26

The crucible in which the ignition of oxide occurred was stained. This was undoubtedly due to the presence of tin, which had not been removed, although hydrogen sulphide had been conducted through the solution of the double fluoride.

Analysis of No. 2 (B):

0.8428 gram of salt gave 0.3635 gram of oxide and
0.4803 gram of potassium sulphate.

0.4811 gram of salt gave 0.2082 gram of oxide and
0.2775[1] gram of potassium sulphate.

$0.3635 : 0.4803 :: x/2 : 174 \qquad x = 263.4.$
$0.2082 : 0.2775 :: x/2 : 174 \qquad x = 250.1.$

	Calculated K_2CbF_7.	Found.	Found.
K_2SO_4	57.05	56.99	57.68
Oxide	43.93	43.13	43.28

[1] Probably too high because it was not heated enough to expel all of the sulphuric acid.

Specific gravity of oxide (B):

18.5924 pyknometer + water, $t = 18°$
.2346 gram of oxide taken
18.8270
18.7760 pyknometer + water + oxide .2346
.0510 gram water displaced .0510 4.60 sp. g.

To determine the titanium content of the columbium oxide recourse was had to a comparison of the color tint produced by hydrogen peroxide in an oxalate solution against known amounts of titanium hydrate dissolved in oxalic acid. Thus, 0.2262 gram of columbium oxide was fused with acid potassium sulphate and the fusion dissolved in oxalic acid and diluted to 50 cubic centimeters. It gave a color equivalent to 0.4 cubic centimeter of the standard titanium solution (1 c.c. contained 0.00106 gram of titanium dioxide). In other words, by this test the columbium oxide was thought to contain 0.000424 gram of titanium dioxide, or .18 %.

Solubility of Crystals A.

One part of the salt was found to be soluble in a little over 12 parts of water. This is the solubility of potassium columbium oxyfluoride.

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100 grams of the residues obtained by the evaporation of mother-liquors (page 180) to dryness were dissolved in water and fractionally crystallized. After having removed as much of the tantalum as possible by introducing dilute potassium hydroxide into the boiling solution until a rather considerable and permanent precipitate was obtained, the solution was boiled for some time. The first fraction of crystals (2) and the third fraction of crystals (3) were removed, after which hydrofluoric acid was added to the mother-liquor, from which there separated a crop of needles, which we shall designate crystals 4. These last were recrystallized from hydrofluoric acid. They probably contained silicon and tantalum. The acid mother-liquors from these different crops of crystals were treated as described by Hermann (*J. pr. Chem.*, Series 2, vol. **15**, 105, 1877). That is, they were treated with 20 parts or two liters of water and 150 grams of sodium hydroxide. A clear solution resulted, from which a fine crystalline precipitate separated. The filtrate from

this precipitate gave no reduction test when treated with acid and zinc, nor was anything obtained from it after having added dilute sulphuric acid and a slight excess of ammonium hydroxide. It was free from earthy bases and metallic acids.

The crystals of the sodium salt (2.5 grams), obtained as outlined in the last paragraph, dissolved almost completely in 20 parts of boiling water and separated in well-defined forms from the cold solution. A portion of this salt heated in a salt of phosphorus bead imparted a blue color to the latter in the reducing flame.

The next step was to decompose the solution of this crystalline sodium salt with dilute sulphuric acid. The solution was hot. The precipitate which separated was thrown upon a filter and washed, after which it was dissolved in hydrofluoric acid and an equivalent amount of potassium carbonate added in order to form potassium columbium oxyfluoride. The solution was evaporated to dryness upon a water bath, the residue repeatedly moistened, and evaporation to dryness repeated until the odor of hydrofluoric acid could not be detected by the smell; then the salt was baked, taken up in water, and the solution boiled for some time. A trace of tantalum oxyfluoride separated. It was filtered out. On evaporation to crystallization the leafy, characteristic crystals of potassium columbium oxyfluoride appeared. They were dried between bibulous paper and then analyzed.

Analysis:

0.5502 gram of salt gave 0.2452 gram of oxide and
0.3224 gram of potassium sulphate

$0.2452 : 0.3224 :: x/2 : 174 \qquad x = 264.6.$

	Calculated $K_2CbOF_3H_2O$.	Found.
Oxide	44.52	44.56
K_2SO_4	57.81	58.60

A portion of crystals No. 4 (page 182) was recrystallized and analyzed.

0.5588 gram of sample gave 0.2407 gram of oxide and
0.3232 gram of potassium sulphate

$0.2407 : 0.3232 :: x/2 : 174 \qquad x = 259.2.$

	Calculated K_2CbF_7.	Found.
Oxide	43.93	43.08
K_2SO_4	57.05	57.84

Analysis of recrystallized portion of crystals (4), page 182.

.5588 gram of sample gave .2407 gram of oxide.

.3232 gram potassium sulphate.

$.2407 : 3232 :: x/2 : 174 \qquad x = 259.2.$

	Calculated. K_2CbF_7.	Found.
Oxide	43.93	43.08
K_2SO_4	57.05	57.84

The results of analysis as well as the behavior points to the fact that the oxide contained in these residues is mainly columbium oxide, Cb_2O_5, with a small portion of another oxide causing the equivalent weights obtained to be too low. These results may in part be due to the presence of some potassium silicofluoride, but more likely to potassium titanium fluoride. Yet these last fractions of double fluoride in which the titanium should be concentrated show only very small amounts. Starting with so much material the last fractions should show more titanium if it is present in the mineral in appreciable amounts.

The only test for small amounts of titanium which we have are the hydrogen peroxide test of Schönn, Jahresberichte, 1893, 901, and the chromotropic acid test used by Geisow (Dissertation, 1902). Of these the former is the only one relied on, and it offers the only direct evidence which we have for the presence of titanium in the potassium columbium oxyfluoride obtained from columbite.

The methods applicable in the preparation of columbium oxide relatively free from titanium are as follows:

1. Crystallization of potassium columbium fluoride (K_2CbF_7) which is not isomorphous with potassium titanium fluoride. The difficulty in this case is that the hydrofluoric acid increases the solubility of the columbium body and decreases that of the titanium double fluoride so that the titanium would have less tendency to concentrate in the mother liquors.

2. Fractional precipitation with dilute ammonium hydroxide. The columbium hydrate is precipitated first and the titanium concentrated in the last fractions. No fraction consists entirely of titanium hydrate; even the last fraction is largely columbium hydrate.

3. The formation of the chloride or oxychloride of columbium and the chloride of titanium and separating these by distillation.

4. Treatment of the hydrates with cold, fairly concentrated sulphuric acid, in which the titanium hydrate should dissolve and leave the columbium.

All of these methods were tried in the endeavor to obtain sufficient titanium from the columbium to identify it and prepare some of its derivatives, *e. g.*, the potassium double fluoride. In order to try out method "1" the remainder of the residues (page 180)—2 to 3 kilos—was crystallized twice from hydrofluoric acid, thus getting potassium columbium fluoride (K_2CbF_7). The mother liquors were united. They equaled 600 c.c. They were neutralized with dilute ammonium hydroxide; the precipitated hydrate filtered out and the filtrate made alkaline with a large excess of ammonium hydroxide, which gave a further precipitate. This last hydrate was filtered out and dissolved in hydrofluoric acid. Potassium carbonate was added and the solution evaporated to dryness on a water bath, the residue taken up in water and crystallized. The crystals obtained were short stubby needles. They were evidently not potassium columbium oxyfluoride (K_2CbOF_5). Their quantity was too small to recrystallize, but they were analyzed:

0.4672 gram of sample gave 0.1740 gram of oxide = 37.6 per cent.
" " " " " 0.3050 gram of K_2SO_4 = 65.3 per cent.

The sp. gr. of the oxide was found to be 5.2, although too little of it was at hand for accurate work. The determination of the titanium in the oxide colorimetrically gave 0.0106 gram of TiO_2 = 6.1 per cent.

The salt originally taken showed 0.62 per cent. of its oxide to be TiO_2 by the colorimetric determination, while the double fluoride of potassium and columbium obtained showed a TiO_2 content equal to .25 per cent. of its oxide. Hence it would seem that by method "1" the titanium or oxide with lower sp. gr. and molecular weight did concentrate in the mother liquors.

Crystals 2 and 3 (page 182) were combined. Their total weight was about one kilo. This, in portions of 100 grams at a time, was dissolved in about 2 liters of water and fractionally precipitated with ammonium hydroxide, using dilute alkali and working in the cold with constant stirring. The alkali was added until the solution was barely acid to litmus, the precipitate formed was filtered off and the filtrate made alkaline with an excess of the precipitant. This

second fraction contained about 3–4 grams of oxide from each 100 grams of double fluoride taken. These ten last fractions were combined and dissolved in hydrofluoric acid, 15 grams of potassium hydroxide added, then dilute ammonium hydroxide until slightly acid, and the precipitate filtered out. It was marked "A." Ammonium hydroxide was then added to the filtrate until litmus showed the reaction to be just neutral. The precipitate was designated "B." "C" was obtained in the filtrate from "B" by adding a large excess of ammonium hydroxide. It (C) presumably should contain most of the titanium from the 1,000 grams of double fluoride taken. The oxide actually present in it was changed to double fluoride by dissolving in hydrofluoric acid and adding potassium carbonate. The first crop of crystals was obtained from strong hydrofluoric acid. It recrystallized from the same in needles. These were analyzed :

0.6954 gram of sample gave 0.3018 gram oxide and
0.3900 gram potassium sulphate,

$.3018 : .3900 :: x/2 : 174, \quad x = 269.3.$

	Calculated K_2CbF_7.	Found.
Oxide	57.05	56.09
K_2SO_4	43.93	43.40

The sp. gr. of the oxide equaled 4.45. 0.3 gram of it showed the presence of the equivalent of .0025 gram of TiO_2, or 0.83 per cent.

The needles from "C," not taken for analysis, and the mother liquor were combined and evaporated to dryness on a water bath to expel the excess of hydrofluoric acid. This was repeated once. The solution of the salt was then fractionally precipitated with amonium hydroxide, the fractions up to the point where litmus showed a slightly alkaline reaction being discarded, when the filtrate from them was made strongly alkaline with ammonium hydroxide. The precipitate obtained was changed to its potassium, double fluoride. About 2.5 grams of the double salt were got.

Analysis :

0.7248 gram of sample gave 0.3014 gram of oxide and
0.4205 gram of K_2SO_4

$0.3014 : 0.4205 :: x/2 : 174 \quad x = 249.4.$

	Calculated $K_2CbOF_5H_2O$.	Found.
Oxide	57.81	58.02
K_2SO_4	44.52	41.58

The sp. gr. of the oxide was found to be 4.667. 0.2930 gram of oxide gave a color with hydrogen peroxide equivalent to .0322 gram of TiO_2 = 11 per cent.

The crucible in which the oxide was ignited was deeply stained. The analysis and the color test showed the presence of titanium, while the stain on the crucible and the high sp. gr. of the oxide could be due to tin in considerable amount, which is precipitated in the last fractions on fractional precipitation with ammonium hydroxide.

The crystals and the mother liquor remaining from this salt were dissolved in boiling water and an excess of sodium hydrate added, when a heavy flocculent precipitate separated. This was filtered, boiled with water and the insoluble portion changed to double fluoride. It was again taken up in boiling water and an excess of sodium hydroxide added. The precipitation was not complete. The portion precipitated was treated with boiling water, filtered, and the filtrate found to contain a large amount of titanium. That portion of the precipitate insoluble in water was changed to double fluoride.

Analysis :

0.5570 gram of sample gave 0.2248 gram of oxide and
0.3468 gram of K_2SO_4

$$0.2248 : 0.3468 :: x/2 : 174 \qquad x = 225.6.$$

The sp. gr. of the oxide was found to be 4.2. The oxide gave a color with hydrogen peroxide showing the presence of about 21 per cent. TiO_2.

Crystals "A" (page 181) were changed to double fluoride and recrystallized.

Analysis :

0.7184 gram of sample gave 0.3188 gram of oxide and
0.4176 gram of potassium sulphate.

$$0.3188 : 0.4176 :: x/2 : 174 \qquad x = 265.7.$$

	Calculated $K_2CbOF_5H_2O$.	Found.
Oxide	44.52	44.38
K_2SO_4	57.81	58.13

The sp. gr. of the oxide was found to be 4.481. 0.3160 gram of oxide gave a color with hydrogen peroxide equivalent to .0022 gram TiO_2 = .7 per cent.

Crystals "B" (page 181) analyzed as follows:

0.8098 gram of sample gave 0.3614 gram of oxide and 0.4708 gram of K_2SO_4

$0.3614 : 0.4708 :: x/2 : 174 \qquad x = 267.0.$

	Calculated $K_2CbOF_5H_2O$.	Found.
Oxide	44.52	44.63
K_2SO_4	57.81	58.14

The sp. gr. of the oxide was found to be 4.864. 0.3600 gram of oxide gave with hydrogen peroxide a color equivalent to .0013 gram of TiO_2 = .36 per cent.

Having failed to get any evidence of the existence of neptunium in the last fractions of the double fluoride from the South Dakota mineral, it was decided to test some of the mineral from Haddam, Conn., the source of the material used by Hermann in his investigation. The last fractions of the potassium double fluoride from 5.87 kilos of columbite from Haddam, Conn., amounting to 100 grams, were dissolved in boiling water and an excess of sodium hydroxide added. The precipitate obtained was partly crystalline and partly flocculent, as described by Hermann. It was filtered out, dried on a porous plate, and boiled with 25 parts of water. The crystals dissolved leaving a yellowish residue evidently containing much iron. This residue gave a yellow colored bead in the reducing flame containing so much iron that it was impossible with a small blowpipe to keep it all reduced. Is it not probable that this is what Hermann supposed was neptunium?

This salt was fused with acid potassium sulphate to remove the iron, the oxide remaining after extracting the fusion with boiling water was changed to double fluoride, dissolved in boiling water, and an excess of sodium hydroxide added. The precipitate obtained was crystalline and perfectly soluble in water, leaving an inappreciable residue. From all of which it may be inferred that

the material from the Haddam locality showed no more evidence of neptunium than did that from South Dakota.

Ten kilograms of the main bulk of the potassium columbium oxyfluoride were crystallized from strong hydrofluoric acid. Five hundred grams were taken at one time and the mother liquors from the two fractions combined, evaporated one half, and another crop of crystals removed. The mother liquors from these were united and evaporated, the crystals obtained were recrystallized, the mother liquors from the recrystallization combined and evaporated to dryness with sulphuric acid. The oxide obtained from that portion evaporated to dryness was 5 grams. The fraction of crystals immediately preceding, 60 grams in weight, was decomposed with sulphuric acid and the oxide obtained from it. The 5 grams of oxide and about one-half of the oxide from the 60 grams of double fluoride were heated in carbon tetrachloride vapors, taking about 2 grams of oxide at a time. The more volatile portion, which should contain the most of the $TiCl_4$, was distilled away from the $CbOCl_3$. The portions of this liquid were combined, the oxides — 3 grams — obtained from it, and these oxides again heated in CCl_4. Again only the liquid portion and that of the solid which was carried over mechanically was taken. The oxide from this portion was changed to double fluoride.

Analysis:

0.5678 gram of sample contained 0.2196 gram of oxide and 0.3390 gram of K_2SO_4.

$$0.2196 : 0.3390 :: x/2 : 174 \qquad x = 225.4.$$

	Calculated $K_2CbOF_5H_2O$.	Found.
Oxide	44.52	38.6
K_2SO_4	57.81	59.7

Amount of TiO_2 in the oxide .0594 gram = 29.7 per cent.

The oxide from the salt taken for analysis was combined with the oxide from the double fluoride not taken for analysis and this with the remaining half of the oxide from the 60 grams of double fluoride mentioned above was mixed with the oxide from all the previous double fluorides which had been tested for titanium and shown its presence in a fair degree. This mixture of oxides was heated in a current of sulphur monochloride, the chloride formed collected

in a receiver, and this was then heated until all of the sulphur monochloride was distilled out. This sulphur monochloride and any other chlorides which it might contain was again distilled to remove the last of the columbium chloride which might have been carried over mechanically. It was then treated with water and oxalic acid, the sulphur filtered off, and any oxide dissolved in the oxalic acid precipitated with ammonium hydroxide. This hydrate was changed to potassium double fluoride.

Analysis :

0.5444 gram of sample gave 0.1952 gram of oxide and
0.3850 gram of potassium sulphate

$$0.1952 : 0.3850 :: x/2 : 174 \qquad x = 175.9.$$

	Calculated. $K_2CbOF_5H_2O$.	Calculated.	Found.
Oxide.....	44.52	33.33	35.85
K_2SO_4.....	57.81	72.50	70.72

0.0310 gram of the oxide was found to contain 0.244 gram TiO_2, or 78.7 per cent.

A solution of the oxide in hydrochloric acid reduced with zinc to an amethyst or violet color ; the oxide also gave a violet titanium bead in the reducing flame with salt of phosphorus.

It would seem that about 80 per cent. of the oxide from this double fluoride was TiO_2.

The remainder of the double fluoride, about .5 gram, was dissolved in the mother liquor from which it came by heating, and an excess of sodium hydrate added. A flocculent precipitate formed. After cooling, this was filtered off and the filtrate acidified with hydrochloric acid and tested for metallic acids with ammonium hydroxide. A precipitate was obtained, which was filtered out and, after washing thoroughly, dissolved in hydrochloric acid.

Upon passing hydrogen sulphide through this solution a heavy precipitate of yellow stannic sulphide was obtained, showing that tin had been carried over with the titanium by the sulphur monochloride.

The precipitate formed by the excess of sodium hydroxide was drained thoroughly and boiled up with water. Nothing went into solution, as would have happened had there been any sodium columbate in the precipitate. This well washed precipitate was

dissolved in hydrofluoric acid and potassium carbonate added to change it to the potassium double fluoride.

Analysis of the crystals obtained:

0.1893 gram of sample gave 0.0642 gram of TiO_2 and 0.1366 gram of K_2SO_4

	Calculated.	Found.
Oxide	33.33	33.91
K_2SO_4	72.50	72.16

The determination of the TiO_2 colorimetrically gave .0636 gram. The salt was undoubtedly potassium titanium fluoride, proving conclusively the presence of titanium in columbite.

Behavior of Solutions of the Double Fluorides of Columbium and of Titanium with a Variety of Bases.

Excess of sodium hydroxide was found to precipitate titanium completely from a solution of potassium titanium fluoride, while with potassium columbium oxyfluoride it gave a precipitate soluble in slight excess but again insoluble and separating in a crystalline form from a large excess of the sodium hydroxide. The precipitate formed in the case of the titanium was insoluble in water, while in the case of columbium the crystalline deposit was completely soluble in hot water. It was hoped that this difference of behavior might afford a means of separating these two elements. To test this experiments were tried as follows:

1. 0.9600 gram of $K_2CbOF_5 + H_2O$, containing 0.4272 gram of Cb_2O_5, and 1.1600 gram K_2TiF_6, containing 0.3753 gram of TiO_2, were dissolved in 200 c.c. water, brought to boiling and an excess of sodium hydroxide added. The precipitate which formed was partly crystalline and partly flocculent. The solution was allowed to stand over night. The precipitate was filtered out, drained, and washed back into a platinum dish. It was covered with 200 c.c. of water, brought to boiling, filtered hot, and washed with hot water. The filtrate which should contain most of the columbium and none of the titanium was brought to boiling and sulphuric acid and ammonium hydroxide added. The hydrate obtained was ignited to oxide and weighed 0.1640 gram. It was found to contain .0117 gram of TiO_2. The titanium content was determined colorimetrically by fusing with potassium acid sulphate, dissolving

the fusion in oxalic acid and comparing the color developed with hydrogen peroxide with that of a titanium solution, of known strength, in oxalic acid.

Part insoluble — 0.2749 Cb_2O_5, 0.3636 TiO_2

$TiO_2 4Cb_2O_5$ soluble portion; $Cb_2O_5 4TiO_2$ insoluble portion.

2. A mixture containing 0.1270 gram K_2TiF_6, or .0423 gram TiO_2 and 2.5280 grams $K_2CbOF_5.H_2O$, or 1.1376 gram Cb_2O_5, was treated as above. The precipitate was nearly all crystalline. That part of it insoluble in water weighed .0470 gram and contained .0074 gram of TiO_2 leaving .0349 gram of TiO_2 in solution (by far the greater quantity).

3. 0.2830 gram K_2TiF_6, containing .0943 gram TiO_2, and 2.7040 grams $K_2CbOF_5H_2O$, containing 1.2168 grams Cb_2O_5, were treated as before. The precipitate was chiefly crystalline. A small part of it was flocculent. The part insoluble in water weighed .0740 gram and contained .0148 gram TiO_2, showing that .0795 gram TiO_2 went into solution and would be found with the bulk of the columbium.

4. 0.6790 gram K_2TiF_6, containing .2263 gram TiO_2, and 2.2530 grams $K_2CbOF_5H_2O$, containing 1.0139 grams Cb_2O_5, were treated as before. The precipitate contained a considerable amount of flocculent material. The part insoluble in water weighed 0.1720 gram and contained 0.0710 gram TiO_2, leaving 0.1553 gram of TiO_2 in solution.

The action of potassium hydroxide was also tried. It gave a precipitate with columbium, soluble in an excess, and reprecipitated by greater excess. When the solution was evaporated pearly plates of potassium columbate separated out. With a solution of K_2TiF_6 a heavy precipitate was obtained, but the filtrate gave a slight test for titanium.

1.3130 gram K_2TiF_6, containing .4377 gram of TiO_2, and 1.0060 gram $K_2CbOF_5H_2O$, containing .4467 gram Cb_2O_5, were dissolved in 200 c.c. of water and the solution brought to boiling, when an excess of potassium hydroxide was added. The precipitate obtained weighed 0.5900 gram after ignition. The filtrate gave a very pronounced test for titanium.

Solutions of K_2TiF_6 and K_2CbOF_5 were studied with various organic bases in the hope that differences of behavior might pre-

sent themselves which would lead to a quantitative separation of these two elements.

Reagent.	Solution of K_2TiF_6.	Solution of K_2CbOF_5.
1. Mono-methylamine,	Precipit. complete,	Precipit. soluble excess.
2. Di-methylamine,	" "	" " "
3. Tri-methylamine,	" "	" " "
4. Tetra-methylamine,	" "	" " "
5. Mono-ethylamine,	" "	" " "
6. Di-ethylamine,	" "	" " "
7. Tri-ethylamine,	" "	" by large excess. insoluble excess. dif. soluble in water.
8. Di-propylamine,	" "	" soluble excess.
9. Amylamine,	" "	" " "
10. Iso-butylamine,	" "	" " "
11. Allylamine,	" "	" " "
12. Ethylenediamine,	" "	" " "
13. Propylenediamine,	" "	" " "
14. Butylenediamine (secondary),	" "	" " "
15. Butylenediamine (normal)	" "	" " "
16. Hexylamine,	" "	" " "
17. Benzylamine,	" "	" " "
18. Benzylmethylamine,	" "	" " "
19. Piperidine,	" "	" " "
20. Camphylamine,	" "	slightly soluble excess.
21. Di-benzylamine,	" "	Precipit. complete.
22. Pyridine,	" "	" "
23. Di-isobutylamine,	" "	" "
24. Tri-propylamine,	" "	" "
25. Di-amylamine,	" "	" "
26. Heptylamine,	" "	" "
27. Toluylenediamine (meta),	Partial precipitation,	" "
28. Picoline,	" "	" "
29. Tri-isobutylamine,	Slight precipitation,	" nearly but not quite complete.
30. Bornylamine,	" "	" not complete.
31. Aniline,	Precipit. not complete,	" heavy but not complete.
32. Toluidine (m),	Slight precipitation,	" " "
33. Mono-methylaniline,	" " after 24 hours,	" " "
34. Mono-ethylaniline,	Slight prec. on standing,	" slow—incomplete.
35. Isoquinoline,	" " "	" heavy—incomplete.
36. Quinoline,	" " "	" nearly complete,

Reagent.	Solution of K_2TiF_6.	Solution of K_2CbOF_5.
37. Hexylmethylenetetramine,	Slight prec. on standing,	Prec. heavy—incomplete.
38. Bromaniline (m),	No precipitation,	Slight prec. on standing.
39. Chloraniline (o),	" "	" " "
40. Di-chloraniline,	" "	" " "
41. Di-ethylaniline,	" "	" " "
42. Chloraniline (p),	" "	" " "
43. Di-methylaniline,	" "	" " "
44. Xylidine (p),	" "	Precipit. slow—incomplete.
45. Xylidine (o),	" "	" " "
46. Xylidine (m),	" "	" " "
47. Tetra-hydroquinoline,	" "	Slight prec. on standing.
48. Benzylaniline,	" "	No precipitation.
49. Di-phenylamine,	" "	" "
50. Tri-benzylamine,	" "	" "
51. Naphthylamine (β),	" "	" "
52. Naphthylamine (α),	" "	" "
53. Nitronaphthalene,	" "	" "
54. Bromphenylhydrazine,	" "	" "
55. Nitrophenylhydrazine,	" "	" "
56. Benzidine,	" "	" "
57. Nitraniline (o),	" "	" "
58. Nitraniline (p),	" "	" "
59. Nitraniline (m),	" "	" "
60. Diphenyl,	" "	" "
61. Diphenyl carbonate,	" "	" "
62. Methyl carbonate,	" "	" "
63. Ethyl carbonate,	" "	" "
64. Piperine,	" "	" "
65. Mono-chlorhydrin,	" "	" "
66 Tri-chlorhydrin,	" "	" "
67. Di-bromhydrin (β),	" "	" "
68. Nitroso-dipropylin,	" "	" "
69. Nitroso-diethylene,	" "	" "
70. Nitroso-dimethylene,	" "	" "
71. Succinimide,	" "	" "
72. Methyl-diphenylamine,	" "	" "
73. Tetra-nitromethylaniline,	" "	" "
74. Bromamiline,	" "	" "

The behavior of the bases which react with the above solutions of titanium and columbium may be divided into the following classes:

1. Those which precipitate the titanium completely, and while they precipitate the columbium dissolve it upon the addition of an

excess of the reagent to form columbates. This class while showing pronounced difference of behavior is useless as a means of separation, for upon treating a solution containing both titanium and columbium with one of these reagents the titanium was found both in the soluble and in the insoluble portion. Columbium was also found in the titanium precipitate. The probable explanation for this is that a columbate was formed which dissolved the freshly precipitated titanium hydrate to a salt of a complex titanoso-columbic acid, which was soluble, and also a small amount of an acid salt or a free acid containing an excess of titanium, which was insoluble.

2. To the second class of reagents belong those which precipitate the hydrates of the two elements and are not sufficiently basic to dissolve the columbium hydrate and form columbates. Those reagents which are sufficiently basic to completely precipitate the columbium are strong enough to partially precipitate the titanium. Quinoline seemed the most promising of all the reagents which were tried.

3. Those reagents which gave only a partial precipitation with columbium and no precipitation with titanium solutions did not precipitate columbium hydrate free from titanium, from a solution containing both titanium and columbium. The hydrate precipitated always gave a strong test for titanium after dissolving it in oxalic acid. This may have been due in part to the extreme difficulty encountered in washing the precipitate free from mother liquor.

4. The remaining reagents precipitated neither titanium nor columbium.

REACTIONS OF THE DOUBLE FLUORIDES OF COLUMBIUM, TITANIUM, TANTALUM, TIN AND TUNGSTEN WITH VARIOUS REAGENTS IN CONCENTRATED SULPHURIC ACID.

A small amount of the reagent was dissolved in eight to ten drops of concentrated sulphuric acid on a glazed porcelain surface and the crystalline double fluoride introduced into this acid solution. In most cases the color was destroyed upon diluting with water. No color was imparted to tin solutions by any of the reagents which appear below.

Reagent.	Ta.	Cb.	Ti.	W.
Codeine,	No color,	No color,	Faint pink; may be due to morphine,	Light brown; on standing trace purple.
Morphine,	Faint yellow,		Red to brown; very delicate,	Gray brown, becoming purple, H_2O ppt.
Resorcinol	No color,	No color,	Red brown; fairly delicate,	No color.
Naphthol (β)	"	Faint yellow brown	Coffee brown; very delicate,	Brown, becoming dark blue.
Naphthol (α)	"	Faint brown,	Green to dark greenish brown,	Deep blue; very delicate.
Pyrogallol,	"	Yellow to light brown,	Dull dark red,	Deep red to brown to dirty blue.
Salicylic acid,	"	Very faint yellow,	Deep red,	Reddish yellow.
Cinchonidine,	"	No color,	No color,	On standing a slight purple.
Apomorphia,	"	Yellow brown,	Light red brown,	Purple to brown to green and blue.
Narceine,	"	Brownish yellow,	Brown,	Dirty dark green.
Bebeerina,	"	No color,	Clear brown,	Dark brown to green.
Narcotina,	"	Yellow,	Brown,	Light brown to green.

Strychnia, quinidia, cinchonidine and atropia gave no color with any of the elements tested. Narceine and bebeerina alone in sulphuric acid gave a considerable color, and with them the amount of reagent used must be very small or it will obscure any change produced by the addition of the double fluoride. In this connection it is of interest to note that Levy (*C. R.*, **103**, 1074 and 1195) studied the colors produced by the phenol-like bodies, dissolved in concentrated sulphuric acid, when brought in contact with the oxides of titanium, tin, tantalum, columbium and other elements, with the following results. Columbium could be tested for in the presence of all the others by using codeine, as it gave a pink color, while titanium yielded no color and tantalum but a faint green. Titanium could be tested for by using morphine, with which it gave a carmine color, columbium no color and tantalum a yellow color passing into brown. Tantalum with resorcinol gave a dirty green color, changing to amethyst and rose, while titanium yielded a flesh red color going to chocolate brown, and columbium a yellowish tint. None of the results were dupli-

cated save the morphine test for titanium, which proved exceedingly delicate, yet to have the color show definitely in columbium the latter must contain .5 per cent. of TiO_2. Codeine gave no color with columbium, nor did resorcinol with tantalum, therefore Levy could not have had pure material for his tests.

In our use of these reagents we failed to find satisfactory tests except in the case of morphine for titanium. None answered for columbium in the presence of titanium or for tantalum in the presence of columbium. Resorcinol proved to be a fairly delicate test for titanium. It gave no color with columbium, tantalum or tungsten.

ACTION OF HYDROCHLORIC ACID GAS ON IGNITED COLUMBIC OXIDE.

0.25 gram of ignited columbic oxide was completely volatilized in three hours in a current of dry hydrochloric acid gas. It volatilized as a white powder with no indication of reduction by change of color. The compound formed adhered to the walls of the glass tube, was insoluble in oxalic acid, and only very slowly soluble in concentrated sulphuric acid, requiring long boiling to dissolve a thin layer. It contained hydrochloric acid, as was shown by washing with ammonium hydroxide and testing the washings with silver nitrate and nitric acid. It would be very difficult to collect in a form convenient for analysis, yet this should be done, as the body evidently contains no water, as is given in the formula of a similar body obtained by Smith and Maas (*Zeit. anorg. Chem.*, **7**, 96) by passing moist hydrochloric acid gas over the hydrated oxide. It is undoubtedly analogous to the body obtained on heating molybdic acid in hydrochloric acid gas, namely, $MoO_3 2HCl$. It is likely $Cb_2O_5.xHCl$.

ACTION OF SULPHURIC ACID ON THE HYDRATES OF COLUMBIUM AND TITANIUM AFTER RECIPITATION BY AMMONIUM HYDROXIDE FROM SOLUTIONS OF THEIR DOUBLE FLUORIDES.

The method used was to precipitate the hydrates from a weighed amount of the double fluorides, filter and wash as thoroughly as possible, then transfer to a weighed platinum dish, reweigh, the difference being water, after which a weighed amount of sulphuric

acid of definite specific gravity was added and allowed to stand in contact with the hydrates for a definite time. The portion insoluble was filtered off, and the amount of oxide going into solution determined by precipitation with ammonium hydroxide, igniting and weighing. The amount of titanium in the oxide which went into solution was determined colorimetrically.

In making these trials columbium oxyfluoride was used in which the titanium oxide as compared with the columbium oxide was .00095 gram TiO_2, or 0.41 per cent. The specific gravity of the sulphuric acid used was 1.145.

EXPERIMENTS.

1. 1 gram of K_2TiF_6, containing 0.3330 gram of TiO_2, was used to obtain the hydrate. The latter was treated with 40 c.c. of water and 70 grams of sulphuric acid. It dissolved completely in fifteen minutes.

2. 0.4450 gram of columbic oxide, in the form of hydrate, was treated with 40 grams of water and 108 grams of sulphuric acid for one hour. Only a slight precipitate was obtained with ammonium hydroxide in the filtrate. It was not weighed but contained .00032 gram of TiO_2, or .07 per cent. of the total oxide taken, or one-sixth of the total TiO_2 present.

3. Columbic hydrate, containing 0.4450 gram of oxide, was treated with 60 grams of water and 123 grams of sulphuric acid for four hours. The portion which dissolved equaled 0.0060 gram = 1.33 per cent., and contained .000424 gram of TiO_2, or 7 per cent. of the oxide dissolved and about one-fourth of the total titanium present.

4. The hydrate from three grams of columbium oxyfluoride, equivalent to 1.35 grams of oxide, was allowed to stand in contact with 50 grams of water and 100 grams of sulphuric acid for seventeen hours. The acid solution showed 0.0236 gram of oxide = 1.75 per cent., containing .000954 gram TiO_2 = 4 per cent. of oxide dissolved or 17 per cent. of the total TiO_2 present.

5. Hydrate containing 0.445 gram of oxide when treated with 57 grams of water and 85 grams of H_2SO_4 (sp. gr. = 1.435) for 45 hours showed in solution 0.0500 gram = 11.1 per cent., containing 0.0008 gram TiO_2 = 1.6 per cent. of the oxide dissolved or 43 per cent. of the total TiO_2 present.

Known amounts of the two hydrates were next treated together as in the following experiments.

6. 0.2816 gram of K_2TiF_6, containing .0939 gram of TiO_2, and 0.5078 gram of $K_2CbOF_5H_2O$, containing 0.2255 gram Cb_2O_5, were treated with 50 grams of water and 15 grams of sulphuric acid (sp. gr. = 1.435) for four hours. The amount of oxide remaining insoluble was only .07 gram. It was not examined as to its titanium content.

7. The hydrate from 0.2420 gram K_2TiF_6, containing .0807 gram TiO_2, and that from 0.3454 gram of $K_2CbOF_5H_2O$, containing 0.1537 gram of Cb_2O_5, were covered with 70 grams of water and 5 grams of sulphuric acid of sp. gr. 1.435. The amount of oxide in solution after four hours was 0.0800 gram, corresponding well with the weight of the oxide of titanium present, but the insoluble portion was found to contain 0.0350 gram of TiO_2, determined colorimetrically; so that only about one-half of the titanium hydrate had been dissolved out while nearly as much columbium hydrate had gone into solution. The acid used would not have dissolved any columbium hydrate had it been free from titanium hydrate; further it would have dissolved out all of the titanium hydrate had it not been mixed with the columbium hydrate. It may, therefore, be concluded that this method of separation is worthless. It remains to be seen how haloid acids would act.

THE CHROMOTROPIC ACID TEST FOR TITANIUM.

Geisow (Dissertation, 1902) observed that the color developed by chromotropic acid with titanium solutions offered a very delicate test for that element. In concentrated solution it gives a deep red, in dilute solutions, a pink color. The color-giving compound was isolated by Geisow and found to have the following composition: one molecule of chromotropic acid to four of TiO_2 and nine of H_2O.

As it was most important to find some means of estimating the amount of titanium in columbium we were induced to study this reaction of Geisow, using solutions of titanic hydrate in oxalic, sulphuric and hydrochloric acids.

Solutions used:

(*A*) 0.53 gram of TiO_2 dissolved in 3.42 grams of oxalic acid and diluted to 500 c.c. 1 c.c. = .00106 gram of TiO_2 and contained .00684 gram of oxalic acid.

(*B*) 10 c.c. of (*A*) diluted to 100 c.c. 1 c.c. = .000106 TiO_2.

(*C*) 10 c.c. of (*B*) diluted to 100 c.c. 1 c.c. = .0000106 TiO_2.

(*D*) 10 grams of oxalic acid in 100 c.c. 1 c.c. = 0.1 gram of oxalic acid.

(*E*) 1 gram chromotropic acid in 100 c.c.

50 c.c. Nessler tubes, one inch in diameter, were used for all of the tests.

.5 c.c. of (*E*) in 50 c.c. of water gave a mere trace of color, for which reason the solution to be tested was always compared with another tube containing the same amount of chromotropic acid, thus making allowance for the slight color given by the solution of that reagent.

.15 c.c. of (*C*) gave a faint pink color when added to 50 c.c. of water containing .5 c.c. of (*E*); .00000159 gram of TiO_2 in 50 c.c. of water gave a change of color; .3 c.c. of the same solution gave a very distinct coloration, or .00000318 gram of TiO_2 in 50 c.c. More than 1 c.c. of the chromotropic acid gave so much color as to interfere with the delicacy of the test.

EFFECT OF OXALIC ACID.

1 c.c. of (*E*).

1 c.c. of (*D*), or 1 gram of oxalic acid in 50 c.c., required 2.6 c.c. of titanium solution (*C*) to show the characteristic pink color, or .0000275 gram of TiO_2.

1 c.c. of reagent was adopted as the amount best suited to use and was the amount taken in all of the following cases unless otherwise stated.

With 0.2 gram of oxalic acid, .0000339 gram of $TiO2_2$ in 50 c.c. gave a pink color.

With 0.5 gram of oxalic acid, .0000275 gram of TiO_2 was required to give the test for titanium.

1.0 gram of oxalic acid required .0000244 gram of TiO_2 to give the test.

In the presence of 2.0 grams of oxalic acid, .0000244 gram of TiO_2 gave a distinct pink color in 50 c.c., while with 5.0 grams of oxalic acid, .0000265 gram of TiO_2 gave a color.

The amount of oxalic acid seems to have little effect although the presence of the acid diminishes the delicacy of the test, but this is independent of the amount of the acid present when more than 0.1 gram is used.

EFFECT OF THE PRESENCE OF HYDROCHLORIC ACID.

The solution of hydrochloric acid used was one part of concentrated acid to five parts of water.

With 1 c.c. of hydrochloric acid (1:5) and 1 c.c. of chromotropic acid in 50 c.c., .0000795 gram of TiO_2 gave a distinct pink color.

With 2 c.c. of hydrochloric acid (1:5) .00017 gram of TiO_2 was required to give the color.

When 5 c.c. of hydrochloric acid (1:5) was used .000424 gram of TiO_2 gave a pink color to 50 c.c.

10 c.c. of hydrochloric acid (1:5) required .000848 gram of TiO_2 for the color.

20 c.c. of hydrochloric acid (1:5) required .00169 gram of TiO_2 in 50 c.c. to give a definite test for titanium.

It may, therefore, be concluded that the destruction of the color given by chromotropic acid is in proportion to the amount of acid present, so if this test is used hydrochloric acid should be absent.

EFFECT OF SULPHURIC ACID.

With 1 c.c. of sulphuric acid, specific gravity, 1.435, 0.000318 gram of TiO_2 was required to give a pink color in 50 c.c. of solution.

With 2 c.c. of sulphuric acid 0.000742 gram of TiO_2 was required to give the titanium test.

While more dilute solutions of sulphuric acid were not tried it is evident that the effect of the sulpuric acid is roughly proportional to the amount of acid present, and that any appreciable amount of this acid seriously interferes with the delicacy of the test. The same is true of hydrofluoric acid.

In the presence of oxalic acid in any appreciable amount chromotropic acid will show .000025 gram of TiO_2 in 50 c.c. very distinctly. Half that amount could be detected but the color is very faint and its similarity to the color possessed by the solution of chromotropic acid itself renders the detection of this amount uncertain. In making the test it is best to avoid the presence of free mineral acids, as they interfere and generally in direct proportion to the amount of acid present. The neutral chlorides and sulphates are without effect, as Geisow has stated. It is probable that the color developed in oxalate solution could be used to determine the

amount of titanium present by comparison with the color developed by known amounts of titanic acid, but this method would offer no especial advantage over the hydrogen peroxide method.

THE ACTION OF CARBON TETRACHLORIDE ON THE OXIDES OF TITANIUM, COLUMBIUM AND TANTALUM.

According to Demarcay (*C. R.*, **104**, 111) carbon tetrachloride vapor passed over the ignited oxides of columbium, titanium and tantalum changes them to chlorides — in the case of titanium with the formation of an intermediate oxychloride.

Lothar Meyer (*Ber.*, **20**, 681) found no action on oxide of titanium. He did not try the other two.

Delafontaine and Linebarger (*Jr. Am. Ch. S.*, **18**, 532) found that oxide of columbium was changed to oxychloride, $CbOCl_3$, with the formation of a small amount of the chloride. In the case of tantalum the oxide was not driven from the boat but remained behind as a pasty mass, suffering no change to chloride. They suggest this as a possible separation of the two elements columbium and tantalum.

The vapor of carbon tetrachloride was found to act slowly on ignited titanic oxide at a low red heat, some chloride of titaninm being continuously formed. In time all of the oxide was converted into chloride.

The oxide of columbium is readily acted upon by carbon tetrachloride even at a low red heat. The principal product is the white oxychloride. Some of the yellow chloride is simultaneously produced. It continues to be formed in small amounts as the oxychloride is sublimed in the vapors of carbon tetrachloride. Columbium oxide heated in a sealed tube with carbon tetrachloride, is completely changed to chloride after several hours at 200°–225°. The chloride dissolves in carbon tetrachloride and separates from it in large, well-formed, needle-like crystals.

The action of the vapors of carbon tetrachloride on ignited oxide of tantalum is rapid, contrary to Delafontaine and Linebarger, converting it into chloride, which can be readily freed from the carbon tetrachloride and thus obtained pure. If the carbon tetrachloride used contains traces of moisture oxide will be produced by the decomposition of the chloride. This oxide dissolves in the fused chloride and remains as a glassy mass upon sublimation of the

chloride. Therefore, care should be taken in the dehydration of the tetrachloride used; otherwise the product will be contaminated with oxide. This seems to be the best method for the preparation of tantalum chloride in large quantities and in a high state of purity. The chloride is an excellent starting-out material for a redetermination of the atomic weight of tantalum, a number none too definite, as a study of the series of results obtained by Marignac (*Zeit. anal. Chem.*, **5**, 478) by the analysis of potassium tantalum fluoride and ammonium tantalum fluoride will show.

The action of carbon tetrachoride on the oxide of columbium also affords an excellent method for the preparation of the oxychloride of that element. It is produced, however, in a very voluminous state, and mats together to a tough felt, completely stopping up any tube used in its preparation. When heated in a sealed tube it condenses on a warm surface to very compact lustrous silky needles. It is very difficult to remove the last traces of columbium pentachloride from this body. This may be done, however, by subliming it in a current of chlorine over ignited oxide, but as long as any carbon tetrachloride is present the columbium chloride will continue to be formed. To make the chloride of columbium it is necessary to have recourse to the action of sulphur monochloride on the oxide or to act on the oxide with carbon tetrachloride in a sealed tube.

PROPERTIES OF COLUMBIUM CHLORIDE.

As already mentioned, columbium chloride is soluble in carbon tetrachloride, forming a yellow colored solution. It is much more soluble when hot than when cold and crystallizes out on cooling in well defined crystals. It is also soluble in sulphur monochloride, the solution saturated in the hot being red in color and depositing yellow crystals of the chloride on cooling. It dissolves in ether with a yellow color. On evaporating this solution on a water bath a thick liquid remains, and an acid vapor is given off, but no crystals separate. Upon ignition the mass chars, then burns and leaves a residue of oxide. On passing dry ammonia gas into the ethereal solution of the chloride a heavy precipitate is formed. This is ammonium chloride and columbium nitride. On washing with water the ammonium chloride is dissolved out, leaving a white residue which reverts on ignition to oxide of columbium, and when boiled

with sodium hydroxide gives off ammoniacal vapors, thus pointing to nitride of columbium, likely Cb_3N_5.

Columbium chloride containing some sulphur monochloride was treated with benzene. The sulphur monochloride dissolved out, while the columbium chloride was decomposed, leaving an insoluble gummy mass. Chloroform dissolved the chloride readily, but the solution seemed to undergo decomposition on warming and evaporating, as the liquid became brown and a brown powder separated. No crystalline product could be procured.

The chloride is also soluble in alcohol. In the cold there is no decomposition. On warming and concentrating the solution acid vapors were given off, due perhaps, as H. Rose has suggested, to the formation of ethyl columbate. That there is no decomposition in dilute solution is shown by the formation of the compound $CbCl_5(C_5H_{11}N)_6$, which was obtained on adding piperidine to the alcoholic solution (*Zeit. anorg. Chem.*, **36**, 100). Other bases, such as aniline, pyridine, etc., gave addition products which were insoluble in the solvent.

The best solvent for columbium chloride is carbon tetrachloride. In this solution reactions should take place, as they do with other chlorides, in aqueous solution; also double chlorides, analogous to the double fluorides, should be formed by bringing together solutions of the chlorides in carbon tetrachloride.

POTASSIUM FLUOXYPERCOLUMBATE.

When potassium columbium oxyfluoride is dissolved in three per cent. hydrogen peroxide the solution acquires a yellow color. When a saturated solution cools a pasty mass of crystals separates. These are very hard to free from mother liquor. When dry they have only a faint yellow tint. On dissolving in water, containing hydrogen peroxide, the solution again becomes yellow in color. The salt obtained in this way is potassium fluoxypercolumbate of the following composition — $K_2CbO_2F_5.H_2O$.

METHOD OF ANALYSIS.

The potassium was determined as sulphate and the columbium as oxide in the usual way, that is, by expelling the fluorine with sulphuric acid, boiling with water, filtering out the insoluble

columbium hydrate and evaporating the filtrate to dryness and weighing the potassium sulphate after ignition.

The oxygen and water were determined in another sample by weighing a portion of the substance in a tube sealed at one end, covering it with a plug of ignited asbestos, connecting with a gas burette and igniting. The oxygen was collected and measured, the tube was reweighed, the loss being water and oxygen. The water was obtained by difference.

Analysis:

0.4004 gram of the salt gave 0.1672 gram of oxide and 0.2196 gram of K_2SO_4

0.4432 gram of the salt lost 0.0470 gram, which contained 17.9 c.c. of oxygen at 24° and under 742 mm. pressure, or 0.0229 gram, the difference — 0.0241 gram — being water.

	Calculated.	Found.
K_2SO_4	54.89	54.84
Oxide	42.28	41.84
O (active)	5.05	5.16
H_2O	5.68	5.44

This salt was obtained and the above composition ascribed to it by Piccini (*Zeit. anorg. Chem.*, **2**, 21). He regarded it as a derivative of percolumbic acid and not an addition product of potassium columbium fluoride and hydrogen peroxide, because the water was lost on heating at 100°, while the oxygen did not escape until the temperature reached 150°.

On crystallizing this salt from concentrated hydrofluoric acid and hydrogen peroxide in the hope of getting a perfluoride large plates were obtained, which were quite yellow in color with a green tint when dry. They did not seem to differ if little or much hydrofluoric acid was used. The crystals taken for analysis were obtained from a solution consisting of one-half hydrofluoric acid, 48 per cent., and one-half hydrogen peroxide, 3 per cent. They were dried between filter paper and promptly weighed out for analysis.

Analysis:

0.7260 gram of salt gave 0.3274 gram of oxide and 0.3982 gram of potassium sulphate.

0.7482 gram of salt lost 0.0784 gram on ignition, i. e., 29.1 c.c. of oxygen at 24° and under 742 mm. pressure, or 0.0374 gram, the difference — 0.0410 gram — being water.

	Calculated.	Found.
K_2SO_4	54.89	54.85
Oxide	42.28	42.34
O (active)	5.05	5.00
H_2O	5.68	5.48

Hence it may be concluded that the salt obtained from strong hydrofluoric acid is the same as that got when hydrofluoric acid is not used.

It would seem impossible to obtain a derivative of percolumbic acid which does not contain oxygen.

The salt separates from solutions containing hydrofluoric acid in large well-formed plates, which may be easily measured. They are much easier to handle than when crystallized from a solution free from acid. The crystals are always greenish yellow in color.

Piccini states that the salt obtained by him had a slight yellow tint, but that this color was completely removed by two recrystallizations from hydrogen peroxide. The salt obtained above was recrystallized six times from hydrogen peroxide containing hydrofluoric acid. The crystals from the last crystallization were fully as highly colored as those which had not been recrystallized. They were then recrystallized twice from hydrogen peroxide containing no acid. The resulting salt was practically colorless, but it dissolved in water and hydrogen peroxide with a yellow color, which was intensified by the addition of hydrofluoric acid and on evaporating again to crystallization the crystals were as highly colored as any obtained previously.

The oxide from the double fluoride, originally used, gave a color equivalent to 0.4 per cent. TiO_2. It was supposed that this color was due entirely to titanium and that the yellow color of the solution and of the crystals of potassium fluoxypercolumbate was also due to this element. To test this supposition 100 grams of the purest potassium columbium oxyfluoride was crystallized twice from strong hydrofluoric acid. The crystals obtained were decomposed with concentrated sulphuric acid, and the hydrate after extraction with water ignited to oxide. The color which this oxide developed in oxalic acid solution with hydrogen peroxide was equivalent

to 0.24 per cent. of its weight of titanic acid. It was now heated in sulphur monochloride and converted into chloride. The latter, together with the excess of monochloride, was collected in a receiver and the sulphur monochloride distilled out in the hope that any titanium tetrachloride present would be expelled with it. The chloride remaining after removing the sulphur monochloride was converted into oxide. It contained titanic oxide equivalent to 0.16 per cent. The oxide was again heated in sulphur monochloride and treated as before. After the second treatment the titanic oxide equivalent was .12 per cent. and the color now developed was different. It was greenish yellow instead of yellow inclining towards red, which is characteristic of titanium. About five grams of the oxide which had passed through this treatment were changed to double fluoride and crystallized from hydrogen peroxide and hydrofluoric acid. Its solution, in hydrogen peroxide, was yellow and its color increased in intensity on adding hydrofluoric acid. The crystals from it were canary yellow with a tint of green, differing in no respect from those previously obtained.

About ten grams of this yellow salt were next dissolved in water and hydrogen peroxide. This solution was distinctly yellow in color. It was divided into two portions. To one portion 0.5 gram of potassium titanium fluoride was added. The color in this portion became considerably deeper, but the excess of color was completely discharged upon adding hydrofluoric acid, the two solutions becoming again identical in color.

Potassium titanium fluoride dissolved in hydrogen peroxide to a deep yellow-colored solution. On cooling crystals were deposited, which were not yellow but colorless when completely free from mother liquor. The addition of hydrofluoric acid to the colored solution completely destroys the color, and in the presence of hydrofluoric acid the salt formed is white, resembling potassium titanium fluoride. When air dried it gives off neither water nor oxygen on ignition.

The only elements which give a distinctive color in acid solution with hydrogen peroxide and which might occur here are titanium, vanadium and molybdenum. Of these the first has been excluded and the second also by reason of the color which it gives (red to rose red). There still remains molybdenum. Its color in an oxalic acid solution with hydrogen peroxide is identical with that

observed in the case of the columbium as free from titanium as it could be obtained. Although the columbium oxide used for these tests had passed through several manipulations which should remove molybdenum, such as, fusion with sodium carbonate and sulphur, changing to chloride with sulphur monochloride and distilling off the more volatile portion, it was thought best to determine how much molybdenum would be required to give a test equal to that obtained from the purest oxide of the columbium at hand. To this end weighed amounts of molybdenum were dissolved in oxalic and sulphuric acids, and the color, developed with hydrogen peroxide, compared with that obtained with a standard titanium solution of hydrogen peroxide.

1. 0.2780 gram of molybdic acid developed a color equivalent to 0.0048 gram TiO_2, or 0.0058 gram of molybdic acid will give a color equal to that given under similar conditions by 0.0001 gram TiO_2.

2. 0.0660 gram of molybdic acid gave a color equal to 0.0015 gram TiO_2, or 0.0044 gram of molybdic acid is equal to 0.0001 gram TiO_2.

The variations in these results is due to the difficulty in matching the different shades as to intensity of color. The average is about right, or 0.0050 gram of molybdic acid is equivalent to 0.0001 gram TiO_2. Calculating on this basis, the best oxide of columbium obtained, which gave a color equivalent to .12 per cent TiO_2, would contain 6 per cent. of MoO_3 if the color was due to the presence of molybdenum, which would be impossible after the treatments through which the oxide has passed. It had been crystallized twice as potassium oxyfluoride, fused with sodium carbonate and sulphur, the tantalum removed, again crystallized as the oxyfluoride of potassium and twice from hydrofluoric as potassium columbium fluoride, then changed to chloride in sulphur monochloride, the sulphur monochloride and the more volatile portions distilled off and rejected, again changed to oxide and this treatment with sulphur monochloride repeated. The final oxide was converted into potassium fluoxypercolumbate and crystallized once from hydrogen peroxide and hydrofluoric acid. This salt was yellow in color, and 0.3540 gram of oxide from it, dissolved in oxalic acid, gave with hydrogen peroxide a color equivalent to 0.000424 gram TiO_2, or .12 per cent. At the most it could not have contained more than a bare trace of oxide of molybdenum.

0.3470 gram of the oxide from the yellow fluoxypercolumbate was dissolved in oxalic acid and chromotropic acid and diluted to 50 c.c. It gave a very slight pink color, about equal in intensity to the color developed in 50 c.c. by .000025 gram TiO_2 in the same amount of oxalic acid on treating with chromotropic acid. This would correspond to less than .01 per cent. of TiO_2 and is likely not very far wrong.

From these experiments it may safely be concluded that the color produced in hydrofluoric acid solution of columbium with hydrogen peroxide is not due to the presence of titanium. Also it is likely that columbium itself gives a distinctive color with hydrogen peroxide, equivalent to from .10 per cent. to .15 per cent. of its weight of TiO_2, yet yellow green instead of straw yellow, as is given by titanium in dilute solutions. Possibly there may still be present some other element. For this careful search will be made.

PREPARATION AND ANALYSIS OF THE YELLOW OXIDE OF COLUMBIUM.

Hydrated oxide of columbium, containing ten grams of oxide, was prepared by decomposing the double fluoride with sulphuric acid, evaporating off the excess of acid and extracting with boiling water. This hydrate was washed repeatedly with boiling water and air dried. It was covered with about 20 c.c. of concentrated hydrochloric acid and brought to boiling for several minutes, until all of the lumps had thoroughly disintegrated, when it was diluted to about three times its original volume with water. All but a few particles were dissolved. This solution was filtered and an equal volume of three per cent. hydrogen peroxide added. It became yellow and after a few minutes a yellow precipitate appeared. The solution was allowed to stand over night. The precipitate was then filtered out, washed with cold water, in which it was insoluble, and air dried.

Under the above conditions about one quarter of the oxide in solution was precipitated by the hydrogen peroxide. If the remainder of the oxide in solution were recovered and dissolved in hydrochloric acid, as before, a fresh portion of it could be precipitated on adding hydrogen peroxide. The air-dried precipitate lost oxygen and water on ignition and regained its white color.

As the precipitation of the columbium was only partial it was best to be certain of the identity of the portion precipitated. To this end 2.5 grams of the yellow oxide were obtained, ignited to remove the excess of oxygen, and changed to the potassium double fluoride. This analyzed as follows:

0.6822 gram of the salt gave 0.3026 gram of oxide and 0.3966 gram of K_2SO_4

	Calculated.	Found.
Oxide	44.52	44.36
K_2SO_4	57.81	58.14

Hence the compound obtained is a derivative of columbium.

Columbium is not precipitated from the solution remaining after the yellow precipitate has been filtered out, by an excess of ammonium hydroxide, until the hydrogen peroxide in the solution has been destroyed.

Analysis of the yellow precipitate:

0.1917 gram of sample gave 0.1298 gram of Cb_2O_5.

0.2556 gram of sample gave 7.8 c.c. of oxygen at 22° and under 741 mm. pressure, equal to 0.0101 gram.

	Percentage.	Ratio.
Cb_2O_5	67.71	1.000
O (active)	3.95	0.984
H_2O (difference)	28.34	6.240
	100.00	

This corresponds to $Cb(OH)_5$, or to $Cb_2O_5H_2O_25H_2O$.

Melikoff and Pissarjewsky (*Zeit. anorg. Chem.*, **20**, 340) obtained a percolumbic acid of the formula $HCbO_4 + nH_2O$, by heating columbium hydrate with 30 per cent. hydrogen peroxide on a water bath. They also obtained it by adding sulphuric acid to a solution of sodium percolumbate, dialyzing out the excess of sulphuric acid and the potassium sulphate, then evaporating the clear yellow solution to dryness on a water bath. They describe it as a yellow amorphous powder, insoluble in water.

The color of these higher oxides seems characteristic of columbium and is certainly not due to the presence of titanium. The hydrate obtained by Melikoff and Pissarjewsky contained twice as much active oxygen, in proportion to the columbium, as did the hydrate obtained during this investigation.

DIFFERENCE IN SOLUBILITY OF DOUBLE FLUORIDES.

It is of interest to note that the solubility of potassium titanium fluoride is increased upon the addition of hydrogen peroxide, while that of the potassium columbium oxyfluoride is decreased. In hydrofluoric acid this order is reversed, the columbium salt becoming more soluble and the titanium salt less soluble. This suggests alternating these solvents in the crystallization of columbium and potassium double fluorides as one of the best means for removing titanium.

Recrystallization from hydrofluoric acid in the form of K_2CbF_7 will remove tin and probably also tungsten from impure potassium columbium oxyfluoride. Two recrystallizations from that solvent are sufficient to give an oxide, the ignition of which in a platinum crucible gave no stain on the crucible. If partially dried oxide wrapped in the filter paper be ignited directly in a platinum crucible the presence of a stain on the crucible after removing the oxide will be a very delicate test for tin. It is likely that when tin is removed by crystallization tungsten is also, if they are present in about equal amounts and in such cases where the total amount is very small. The procedure would remove the necessity for the tedious sodium carbonate and sulphur fusions used in this work.

BEHAVIOR WITH PRECIPITANTS.

Pennington (*Jour. Amer. Chem. Soc.*, **18**, 38) noted that disodium hydrogen phosphate gave no precipitate in a solution of potassium columbium oxyfluoride, while it completely precipitated titanium from a solution of its double fluoride. This was studied briefly in order to determine if it might not serve as a quantitative separation of columbium from titanium. It was found that when the reagent was added to a solution containing a large excess of columbium and only a little titanium no precipitate was produced even on prolonged boiling. If the amount of titanium was increased slightly both the titanium and the columbium were completely precipitated by the disodium hydrogen phosphate. This reagent, therefore, does not separate the two elements.

Geisow found that an alkaline formoxime solution precipitated zirconium and titanium, but did not precipitate columbium.

Formoxime, or its polymerization product, was prepared by bringing together solutions of the calculated quantities of formal-

dehyde, sodium carbonate, and hydroxylamine hydrochloride. The resulting solution gave no precipitate when added to a solution of titanium as double fluoride, zirconium as double fluoride, or to a solution of columbium double fluoride. Further, after the addition of the formoxime solution, ammonium hydroxide failed to give a precipitate with any of the solutions noted above. It did, however, give a precipitate with tantalum double fluoride, but this was only partial.

The statement of Geisow that titanium and zirconium can be separated from columbium by means of an alkaline formoxime solution was not verified. The precipitation with tantalum is only partial, and not complete as stated by him.

It was noted (*Jour. Amer. Chem. Soc.*, **26**, 1248) that potassium iodate gave a complete precipitation in a solution of potassium titanium fluoride, and no precipitate with a solution of columbium double fluoride. Potassium iodate, free from periodate, was prepared, and it was found to give no precipitate with either columbium or titanium, except in acid solution, when both were precipitated. A solution of a periodate was not tried.

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